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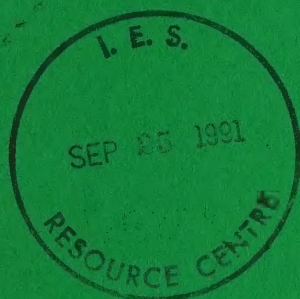
# POLYCHLORINATED NAPHTHALENES SURVEY

AT

GOODYEAR (OWEN SOUND HARBOUR)  
OCTOBER 16-19, 1990



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**POLYCHLORINATED NAPHTHALENES SURVEY AT GOODYEAR  
(OWEN SOUND HARBOUR) OCTOBER 16-19, 1990.**

Report prepared by:

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Water Resources Branch

Ontario Ministry of the Environment

SEPTEMBER 1991



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## FOREWORD

In April, 1990, an oily sheen observed in Owen Sound Harbour near the Goodyear V-Belt Plant led to sampling of the plant's effluent by local Ontario Ministry of the Environment (MOE) staff. Although initially identified as polychlorinated biphenyls (PCBs), subsequent analysis showed that the contaminant was in fact polychlorinated naphthalenes (PCNs).

Available information indicated that some PCNs are strong irritants, have the potential to accumulate in organisms and persist in the environment, and are toxic to certain marine test organisms. There were, however, no available criteria or objectives for PCNs, nor any information on the effects on freshwater species from which such values could be derived for the Province of Ontario.

Consequently, a study was initiated in October, 1990 by the Watershed Management-Bioassessment and the Great Lakes Sections of the Ministry's Water Resources Branch to obtain information on the toxicity of PCNs and the impact of the Goodyear discharge on nearby Owen Sound Harbour water, sediment and biota.

This report provides a summary and assessment of data obtained during the October 16-19 Great Lakes Section survey of the environmental impacts of PCNs discharged into Owen Sound Harbour by the Goodyear V-Belt plant. Although findings of the Watershed Management-Bioassessment surveys and bioassays are also referred to in this report, the actual data or reports are available through that section.

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- E. Timmer (GLS) for typing of the manuscript.





## EXECUTIVE SUMMARY

To address concerns about the aquatic impacts of polychlorinated naphthalenes (PCNs) discharged by the Owen Sound Goodyear V-Belt Plant, a survey was conducted by the Ministry's Great Lakes Section in October, 1990. The objectives were:

- i) to determine the extent and degree of contamination of Owen Sound Harbour in the vicinity of the Goodyear plant by PCNs and other trace organic and metal contaminants; and
- ii) to determine the impact of sediment contamination on both the resident benthic community as well as on laboratory test organisms.

The study involved the collection of water, sediment, benthic macroinvertebrate and selected discharge samples, and the exposure of biological monitors (mussels) in cages.

### Polychlorinated Naphthalenes

Four discharges to Owen Sound Harbour were sampled using large volume (18 litre) containers: the Goodyear plant's final effluent (immediately after granular activated carbon treatment), the nearby 32nd St. E. storm sewer and Kenny Drain, and the Owen Sound Water Pollution Control Plant final effluent. PCNs were only detected in the Goodyear effluent, at 13 ng/litre (parts per trillion). Although flow of this discharge was not continuous during the survey, if one uses the annual average daily flow, this concentration would result in a daily loading of about 10 g/day that would not be detectable through routine sampling and analytical methods. Currently, PCNs are being sporadically detected in the Goodyear final effluent discharge (on shore) at levels of 20 to 50 ng/l, and this may be due to the purging of residual contamination from the sewer system. Accordingly, it is recommended that, if there is a need to determine PCN loadings during this process, then periodic large volume sampling of the Goodyear effluent should be conducted.



## **EXECUTIVE SUMMARY** (cont'd)

No PCNs were detected in any of the routine (1 litre) or large volume Owen Sound Harbour water samples collected upstream or downstream of the Goodyear plant discharge. Also, PCNs were not found in any surficial sediment samples, indicating that the impact of the PCN losses was minimal. Caged mussel tissue samples have not yet been analyzed. However, since low levels of PCNs were found in some young-of-the-year minnow samples collected near the plant, it is recommended that the mussels be analyzed to aid in further defining the impact of the Goodyear discharge.

### **Other Organochlorine Contaminants**

Although PCBs, organochlorine pesticides and chlorinated benzenes were also analyzed for in discharge, water and sediment samples, only low concentrations ( $\leq 2$  ng/litre) of alpha- and gamma BHC were found in the aqueous samples. These two BHC isomers are relatively ubiquitous in the Great Lakes and no local source was implicated.

### **Polycyclic Aromatic Hydrocarbons**

Low concentrations (2-12 ng/l) of phenanthrene, fluoranthene, pyrene and benzo(a)anthracene were found in most of the large volume Owen Sound Harbour water samples. The detection of most of the above compounds in the Goodyear effluent and in the nearby 32nd St. E. storm sewer discharge suggests that these are the probable sources. However, it should be noted that PAHs may not have been detected in the other two discharges sampled due to a very high hydrocarbon background which resulted in ten-fold higher detection limits for these components. Although PAHs were not detected in surficial sediments, it is recommended that the caged mussel samples be analyzed to determine whether or not the PAHs are biologically available and constitute a problem.



## EXECUTIVE SUMMARY (cont'd)

### Nutrients and Trace Metals

Concentrations of nutrients and trace metals in surficial sediments were quite low, and under the current MOE dredging guidelines, the sediments would be considered to be safe for open water disposal. At some stations, however, phosphorus, nitrogen, copper and nickel concentrations were slightly above the recently-proposed (draft) lowest effect level guidelines for the protection of the majority of sediment-dwelling organisms. In laboratory tests, sediments from selected stations were toxic to young fathead minnows, and this is believed to be due to ammonia released from the sediments.

### Other Parameters

Elevated conductivity, suspended solids, calcium, chloride and dissolved organic carbon levels were found in nearshore water samples after heavy rainfall events. The spatial pattern is indicative of sources other than Goodyear, in particular the Kenney Drain discharging south-west of the plant. It is recommended that the impact of this periodic large input of particulates on the aquatic environment and biota be investigated, and that measures to reduce the loading be initiated.





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## **1.0 BACKGROUND**

### **1.1 Site Description**

Owen Sound is located in the south-west end of Georgian Bay (Figure 1). Situated in a U-shaped valley on the Bruce Peninsula, it is mainly bordered by the Niagara Escarpment which is located some 1 to 5 km inland, and along the north-east, by shore bluffs of ancient Lake Algonquin. The Algonquin lake bed around Owen Sound consists of wave-swept shelves of sandstone and shale (Chapman and Putnam, 1973) and is therefore largely non-depositional (IJC, 1977).

Two small rivers, the Sydenham and the Pottawatomi, originate south and west of Owen Sound and empty into its southern end (Figure 1). A number of storm sewers discharge to these rivers (Kleinfeldt, 1987) as they pass through the City of Owen Sound. Combined daily flow of these two rivers averages about  $500 \times 10^3 \text{ m}^3/\text{d}$ .

The City of Owen Sound (Grey County), with a population of approximately 20,000, borders the southern end of the Sound. Owen Sound Harbour extends from the southern end of the Sound north to a line between Bayview Point and Squaw Point (Figure 1), and is situated on a sand plain. Although farming and animal production are important industries in the surrounding area, several manufacturing plants are located in the city, and oil storage tanks and a large grain elevator dominate the southern end of Owen Sound Harbour.

### **1.2 Previous Studies**

MOE studies of Owen Sound Harbour during the period 1974 to 1979 (MOE, 1980) found that most of the Harbour was relatively pollution-free. Waters usually had low chlorophyll concentrations and were of good clarity, with Secchi disk depths averaging 3.9 to 6.2 m. Moderately degraded waters were, however, associated with the mouths of the Sydenham and Pottawatomi Rivers and the Owen Sound Water Pollution Control Plant (WPCP) outfall. (The latter is presently a primary plant with continuous phosphorus removal and sludge digestion.) Waters at the mouths of both rivers contained high densities of bacteria, and the mouth of the Pottawatomi River also had elevated phosphorus levels. Near the WPCP, surface



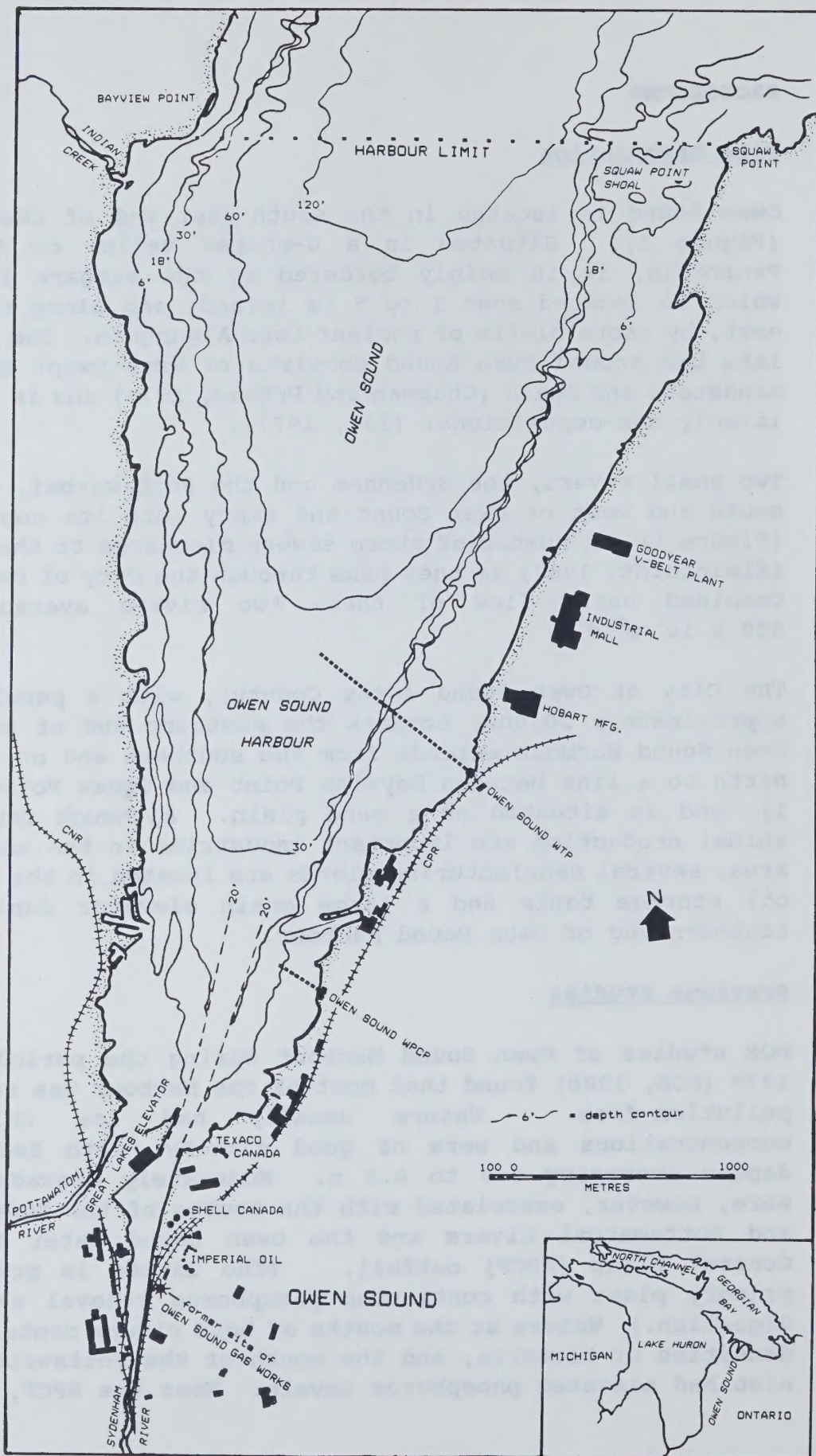


Figure 1. Owen Sound Harbour bathymetry and major municipal and industrial facilities.



waters periodically had high phosphorus, free ammonia and phenols concentrations. The poorest sediment quality (as reflected by exceedences of the provincial guidelines for open water disposal of dredged material for copper, iron, lead, zinc, loss on ignition and oils and greases) was found at the mouth of the Sydenham River, with less contaminated sediments being found northward along the eastern shoreline and in deeper water (MOE, 1980).

Large standing stocks of organic pollution-tolerant tubificid worms were found in the sediments of lower Owen Sound (Barton & Carter, 1974 as cited in Barton & Griffiths, 1984). However, an MOE study in 1980 indicated that enriched sediments did not extend further northward into the Sound, since pollution-tolerant species never dominated the benthic fauna there (Barton & Griffiths, 1984).

During the years 1888-1947, a coal gasification plant was located in the City of Owen Sound beside the Sydenham River (Intera, 1987 and Figure 1). A site-specific study was conducted by the present owners of the property and by the MOE, and it was found that migration of polycyclic aromatic hydrocarbons (PAHs) to the river was possible via storm sewer sediments. Sewers were cleaned out in March, 1991 and both the accumulation and quality of sediment in them will be monitored on a long-term basis (W. Page, MOE, Owen Sound, pers. comm., 1991). Furthermore, in 1990, an in-place pollutants study focused on the impact of coal tar (containing PAHs) on the local aquatic environment. Results of this MOE study are not yet available.

### **1.3 The Polychlorinated Naphthalenes Issue**

In April, 1990 the presence of an oily sheen in Owen Sound Harbour led to sampling of the Goodyear V-Belt Plant effluent by MOE District Office staff. Although initially identified as PCBs, subsequent analysis determined that the pollutant was in fact polychlorinated naphthalenes (PCNs), mainly isomers of trichloronaphthalene and tetrachloronaphthalene. Overall, the PCN mixture most closely resembled Halowax 1099, which also contains di- and pentachloronaphthalene isomers (MOE - Hazardous Contaminants Branch (HCB), internal memo, 1990).



Available information indicates that tri- and tetrachloronaphthalenes are toxic by ingestion, inhalation and skin absorption, and are strong irritants (MOE-HCB, internal memo, 1990). Tests with Halowax 1099 and the marine shrimp Palaemonetes pugio showed that PCNs are also toxic to aquatic life; the 96 hr LC<sub>50</sub> of Halowax was 69 µg/l (Verschueren, 1983). The low water solubility of tri- and tetrachloronaphthalenes, combined with estimated octanol-water partition coefficients of 5.43 and 6.14, respectively, suggests that they may readily be adsorbed by organic-containing particulate matter or accumulate in the lipids of organisms. For example, a bioaccumulation factor of 257 resulted after 3 days' exposure of P. pugio to 40 µg Halowax 1099/l (Vershueren, 1983). Although they would also be expected to persist in the environment, studies have shown that PCNs degrade in the presence of light (MOE - HCB, internal memo, 1990).

## 2.0 STUDY OBJECTIVES

Objectives of this study were:

- i) to determine the extent and degree of contamination of Owen Sound Harbour in the vicinity of the Goodyear V-Belt Plant by polychlorinated naphthalenes and other trace organic and metal contaminants; and
- ii) to determine the impact of sediment contamination on both the resident benthic community as well as on laboratory test organisms.



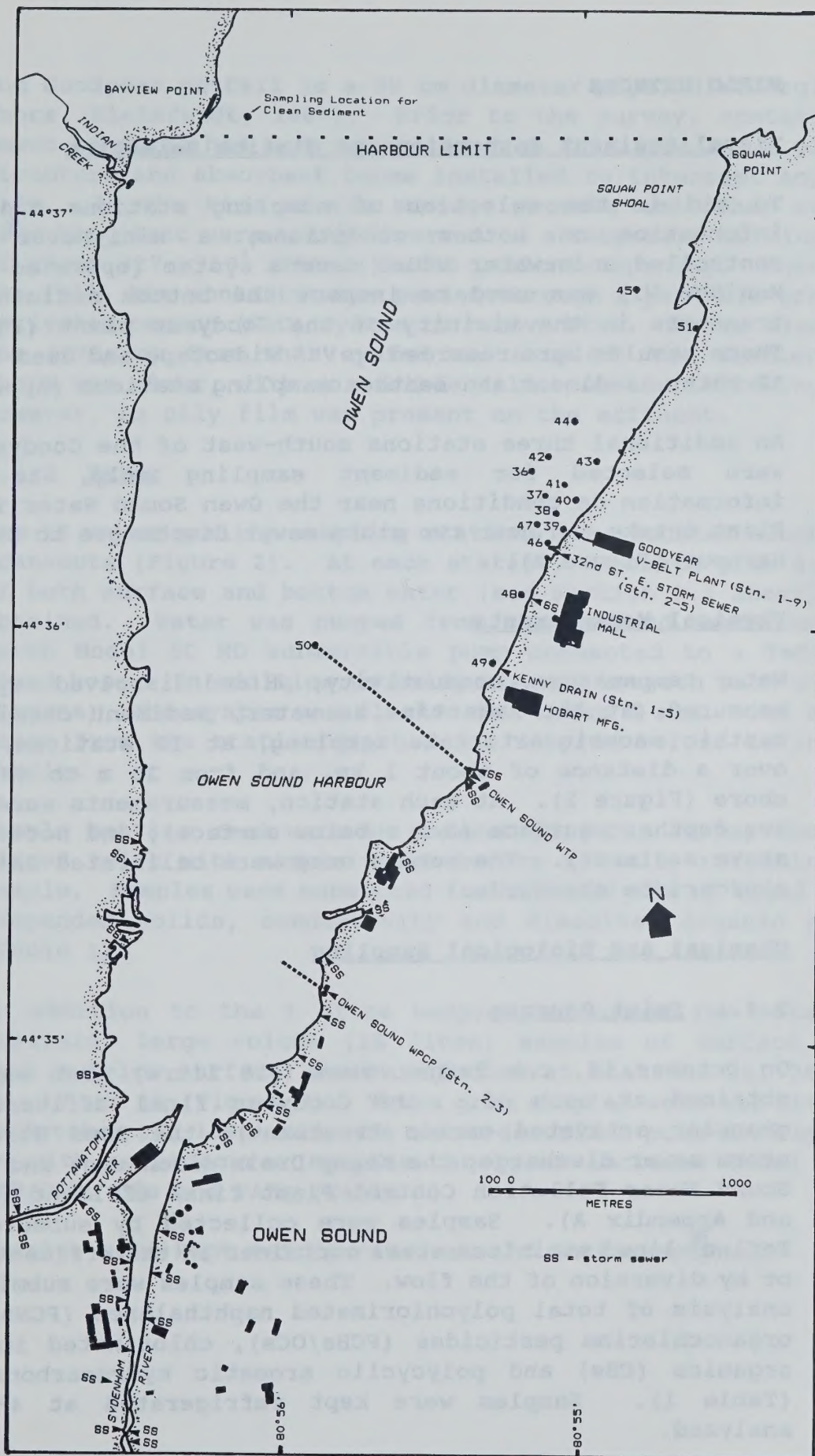


Figure 2. Location of Owen Sound Harbour sampling stations.



### **3.0 FIELD METHODS**

#### **3.1 Visual Sediment Inspection and Station Selection**

To aid in the selection of sampling stations and provide information on bottom conditions, a Mini-Rover<sup>®</sup> remote-controlled underwater video camera system (operated from the Monitor VI) was used to inspect the bottom sediments along transects in the vicinity of the Goodyear plant (Figure 2). These results were recorded on VHS videotape and used to select 12 water, sediment and benthos sampling stations (Appendix A).

An additional three stations south-west of the Goodyear plant were selected for sediment sampling only, to provide information on conditions near the Owen Sound Water Treatment Plant intake and near two storm sewer discharges to Owen Sound Harbour (Figure 2).

#### **3.2 Physical Measurements**

Water temperature, conductivity, pH and dissolved oxygen were measured (at the same time as water, sediment chemistry and benthic macroinvertebrate sampling) at 12 stations, ranging over a distance of about 1 km, and from 30 m to 400 m from shore (Figure 2). At each station, measurements were made at two depths: surface (0.1 m below surface); and bottom (0.2 m above sediment). The meters used were calibrated daily using appropriate standards.

#### **3.3 Chemical and Biological Sampling**

##### **3.3.1 Point Sources**

On October 18, one large volume (18 litre) grab sample was obtained at each of: the Goodyear final effluent (after granular activated carbon treatment); the 32nd Street East storm sewer discharge; the Kenny Drain discharge; and the Owen Sound Water Pollution Control Plant final effluent (Figure 2 and Appendix A). Samples were collected by submerging the Teflon<sup>®</sup>-lined stainless steel container in the effluent stream, or by diversion of the flow. These samples were submitted for analysis of total polychlorinated naphthalenes (PCNs), PCBs/organochlorine pesticides (PCBs/OCs), chlorinated industrial organics (CBs) and polycyclic aromatic hydrocarbons (PAHs) (Table 1). Samples were kept refrigerated at 4°C until analyzed.



The Goodyear outfall is a 55 cm diameter pipe, discharging on shore (Kleinfeldt, 1987). Prior to the survey, contaminated beach material had been excavated from this area and a plywood structure and absorbent booms installed to intercept any oily film. At the time of the survey, process and other streams from the plant were being diverted to a temporary holding pond of about  $227 \times 10^3$  litre (50,000 gallon) capacity. When this was full, the contents were passed through a portable granular activated carbon (GAC) system to remove PCNs. At the time that the effluent from this system was sampled, the discharge on shore was clear, with no visible film. On the following day, however, an oily film was present on the effluent.

### 3.3.2 Water

The 12 water quality sampling stations were located along five transects (Figure 2). At each station, separate grab samples of both surface and bottom water (see Section 3.2 above) were obtained. Water was pumped from the desired depth using a March Model 5C MD submersible pump connected to a Teflon<sup>®</sup>-lined hose. In addition to being cleaned between each station (hexane), the system was flushed for about 5 min. with sample water from the station/depth being sampled before taking any sample.

Sample bottles used were as prescribed (MOE, 1989a) and were rinsed twice with sample water before actually retaining the sample. Samples were submitted for the analysis of total PCNs, suspended solids, conductivity and dissolved organic carbon (Table 1).

In addition to the 1 litre samples submitted for total PCN analysis, large volume (18 litre) samples of surface water (0.1 m below surface) were collected at stations 39, 38, 40, 43, 46 and 45 (Figure 2). These grab samples were all obtained on October 17, 1990 using the above-described pump-hose system. As with point-source samples, analyses included total PCNs, PCB/OCs, CBs and PAHs (Table 1).

Samples were kept refrigerated at 4°C until analyzed.



Table 1. Summary of sample analytical requests.

| Parameter                                         | Point Source<br>(large volume) | Water<br>(conventional) | Water<br>(large volume) | Surficial Sediment<br>& Sludge |
|---------------------------------------------------|--------------------------------|-------------------------|-------------------------|--------------------------------|
| <u>Physical &amp; Miscellaneous:</u>              |                                |                         |                         |                                |
| Conductivity @25C                                 |                                | x                       |                         |                                |
| Calcium                                           |                                | x                       |                         |                                |
| Chloride                                          |                                | x                       |                         |                                |
| Suspended Solids                                  |                                | x                       |                         |                                |
| Particle Size Distribution                        |                                |                         |                         | x                              |
| <u>Nutrients:</u>                                 |                                |                         |                         |                                |
| Dissolved Organic Carbon                          |                                | x                       |                         |                                |
| Loss on Ignition                                  |                                |                         |                         | x                              |
| Total Organic Carbon                              |                                |                         |                         | x                              |
| Total Kjeldahl Nitrogen                           |                                |                         |                         | x                              |
| Total Phosphorus                                  |                                |                         |                         | x                              |
| <u>Trace Metals (unfiltered total):</u>           |                                |                         |                         |                                |
| Arsenic                                           |                                |                         |                         | x                              |
| Cadmium                                           |                                |                         |                         | x                              |
| Chromium                                          |                                |                         |                         | x                              |
| Copper                                            |                                |                         |                         | x                              |
| Iron                                              |                                |                         |                         | x                              |
| Lead                                              |                                |                         |                         | x                              |
| Mercury                                           |                                |                         |                         | x                              |
| Nickel                                            |                                |                         |                         | x                              |
| Zinc                                              |                                |                         |                         | x                              |
| <u>Solvent Extractables (Oil &amp; Grease):</u>   |                                |                         |                         | x                              |
| <u>Total Polychlorinated Naphthalenes (PCNs):</u> | x                              | x                       | x                       | x                              |
| <u>PCBs/Organochlorine Pesticides (PCBs/OCs):</u> |                                |                         |                         |                                |
| <u>Total Polychlorinated Biphenyls (PCBs)</u>     | x                              |                         | x                       | x                              |
| Aldrin                                            | x                              |                         | x                       | x                              |
| Dieldrin                                          | x                              |                         | x                       | x                              |
| alpha-BHC                                         | x                              |                         | x                       | x                              |
| beta-BHC                                          | x                              |                         | x                       | x                              |
| gamma-BHC (Lindane)                               | x                              |                         | x                       | x                              |
| alpha-Chlordane                                   | x                              |                         | x                       | x                              |
| gamma-Chlordane                                   | x                              |                         | x                       | x                              |
| p,p'-DDD                                          | x                              |                         | x                       | x                              |
| p,p'-DDE                                          | x                              |                         | x                       | x                              |
| o,p'-DDT                                          | x                              |                         | x                       | x                              |
| p,p'-DDT                                          | x                              |                         | x                       | x                              |
| Endrin                                            | x                              |                         | x                       | x                              |
| alpha-Endosulphan (Thiodan I)                     | x                              |                         | x                       | x                              |
| beta-Endosulphan (Thiodan II)                     | x                              |                         | x                       | x                              |
| Endosulphan Sulphate                              | x                              |                         | x                       | x                              |
| Heptachlor                                        | x                              |                         | x                       | x                              |
| Heptachlor epoxide                                | x                              |                         | x                       | x                              |
| Oxychlordane                                      | x                              |                         | x                       | x                              |
| Methoxychlor (DNMT)                               | x                              |                         | x                       | x                              |
| Mirex                                             | x                              |                         | x                       | x                              |



Table 1. Summary of sample analytical requests. (continued)

| Parameter                                       | Point Source<br>(large volume) | Water<br>(conventional) | Water<br>(large volume) | Surficial Sediment<br>& Sludge |
|-------------------------------------------------|--------------------------------|-------------------------|-------------------------|--------------------------------|
| <u>Chlorobenzenes (CBs):</u>                    |                                |                         |                         |                                |
| Hexachlorobutadiene (HCBD)                      | X                              |                         | X                       | X                              |
| Hexachloroethane (HCE)                          | X                              |                         | X                       | X                              |
| Hexachlorobenzene (HCB)                         | X                              |                         | X                       | X                              |
| Pentachlorobenzene (QCB)                        | X                              |                         | X                       | X                              |
| 1,2,3,4-Tetrachlorobenzene (TeCB)               | X                              |                         | X                       | X                              |
| 1,2,3,5-Tetrachlorobenzene                      | X                              |                         | X                       | X                              |
| 1,2,4,5-Tetrachlorobenzene                      | X                              |                         | X                       | X                              |
| 1,2,3-Trichlorobenzene (TCB)                    | X                              |                         | X                       | X                              |
| 1,2,4-Trichlorobenzene                          | X                              |                         | X                       | X                              |
| 1,3,5-Trichlorobenzene                          | X                              |                         | X                       | X                              |
| 2,3,6-Trichlorotoluene (TCT)                    | X                              |                         | X                       | X                              |
| 2,4,5-Trichlorotoluene                          | X                              |                         | X                       | X                              |
| 2,6,a-Trichlorotoluene                          | X                              |                         | X                       | X                              |
| Octachlorostyrene (OCS)                         | X                              |                         | X                       | X                              |
| <u>Polycyclic Aromatic Hydrocarbons (PAHs):</u> |                                |                         |                         |                                |
| Acenaphthene                                    |                                |                         |                         | X                              |
| Acenaphthylene                                  |                                |                         |                         |                                |
| Anthracene                                      | X                              |                         | X                       | X                              |
| Benzo(a)Anthracene                              | X                              |                         | X                       | X                              |
| Benzo(b)Fluoranthene                            | X                              |                         | X                       | X                              |
| Benzo(k)Fluoranthene                            | X                              |                         | X                       | X                              |
| Benzo(g,h,i)Perylene                            | X                              |                         | X                       | X                              |
| Benzo(a)Pyrene                                  | X                              |                         | X                       | X                              |
| Chrysene                                        | X                              |                         | X                       | X                              |
| Coronene                                        | X                              |                         | X                       |                                |
| Dibenzo(a,h)Anthracene                          | X                              |                         | X                       |                                |
| Dimethyl(a)Anthracene                           | X                              |                         | X                       |                                |
| Fluoranthene                                    | X                              |                         | X                       | X                              |
| Fluorene                                        |                                |                         |                         | X                              |
| Indeno(1,2,3-cd)Pyrene                          | X                              |                         | X                       | X                              |
| Naphthalene                                     |                                |                         |                         | X                              |
| Phenanthrene                                    | X                              |                         | X                       | X                              |
| Perylene                                        | X                              |                         | X                       |                                |
| Pyrene                                          | X                              |                         | X                       | X                              |



### 3.3.3 Surficial Sediment

Surficial sediment samples were collected at each of 15 stations (Figure 2) using a solvent (hexane)-rinsed Shipek dredge. The central, top three centimetres of sediment from each of at least three grabs was removed using a solvent-rinsed stainless steel spoon. At all but four of these stations (see section 3.4.2), these replicates were then homogenized in a solvent-rinsed stainless steel pan.

After dividing the sample(s) from each station among the appropriate containers (MOE, 1989a), sediments were submitted for analysis of total PCNs, PCBs/OCs, CBs, PAHs, solvent extractables (oil and grease), trace metals, nutrients and particle size distribution (Table 1).

Samples were kept refrigerated at 4°C until analyzed.

### 3.3.4 Sediment Bioassays

At four selected locations near the Goodyear discharge (stations 39, 38, 40 and 46), about 15 litres of additional surficial sediment material was collected with a clean Shipek dredge for laboratory sediment toxicity testing using Hexagenia nymphs, Chironomus larvae and fathead minnows (Pimephales promelas).

Two piles of contaminated material that had previously been excavated from the shoreline in front of the Goodyear discharge were also sampled for toxicity testing. (Prior analysis of this material found a total PCN concentration of 71 mg/kg (MOE-HCB, internal memo, 1990). From each, about 15 litres of material, composed of seven grabs taken from the periphery of the pile, was collected.

Finally, 15 litres of clean, soft sediment was obtained from deeper water off Bayview Point for possible later spiking bioassays (Figure 2).

The bioassay sediment from each station or site was placed in a pre-cleaned 25 litre plastic pail lined with a food-grade polyethylene liner, closed and kept cool, and delivered to the MOE Watershed Management - Bioassessment Lab in Rexdale.



### **3.3.5 Benthic Macroinvertebrates**

The benthic macroinvertebrate community was sampled at the same 12 stations as those used for water and sediment quality (Figure 2). At each station, three replicate sediment grabs were obtained using a Ponar dredge.

Organisms in each replicate were immediately separated from the sediments by placing the sample in a combination 200  $\mu\text{m}$ /600  $\mu\text{m}$  nylon mesh bag (600  $\mu\text{m}$  bag on the inside) and washing with harbour water. Organisms retained by the two different mesh sizes were then individually preserved in glass jars with buffered (pH 7) formalin. This resulted in six samples of benthos per station for subsequent identification and enumeration, if deemed necessary after evaluation of the initial analytical results (see section 5.0).

### **3.3.6 Caged Mussel Biomonitoring**

Of the 12 water and sediment quality sampling stations, six in the immediate vicinity of the Goodyear plant were selected for biomonitoring using the freshwater mussel Elliptio complanata, obtained from a population in Balsam Lake. These included stations 39, 38, 40, 43, 46 and 45. An additional station (number 51), in the nearshore of an embayment north-east of Goodyear, was also monitored (Figure 2).

At each of the seven stations, 15 mussels of a uniform size class (6.5 - 7.2 cm long) were distributed among two clean, galvanized wire cages, each with dimensions of about 30 cm x 36 cm x 10 cm. This number of individuals was sufficient for the analysis of three replicates for each of the scans or test groups noted below. The cages were then anchored to the bottom, using rope attached to a concrete block. Background, or pre-exposure concentrations of contaminants in mussels were determined by processing (as described below) randomly-selected individuals from the Balsam Lake collection prior to their transport to Owen Sound.

After an exposure period of 23 days (Oct. 17 - Nov. 9), all cages were retrieved and the mussels immediately shucked using a solvent (hexane)-rinsed knife. The soft tissues of each mussel were rinsed with clean water, the fresh (wet) tissue weight recorded and then individually wrapped.



Mussels designated for total PCNs, PCBs/OCs, CBs and PAHs analysis were first wrapped in solvent (hexane)-rinsed aluminum foil before placing in a plastic Whirl Pac<sup>(R)</sup> bag. Mussels for trace metals analysis were placed directly in a clean Whirl Pac bag. Mussels were then frozen (-20°C) until analyzed, if this was deemed necessary.

### **3.4 Field Quality Assurance**

#### **3.4.1 Water**

At two stations randomly selected from the 12, three replicate water samples were collected (at one depth only) to provide data on within-station variability.

At these two stations, blind duplicate ("split") samples were obtained at one of the depths. Also, two "field blanks" were obtained by pouring distilled water through the pump-hose collection system to provide information on potential station-to-station cross-contamination. Finally, one set of bottles was filled with distilled water. These served as a "travel blank" to determine potential background (container) contributions to the observed concentrations.

#### **3.4.2 Surficial Sediment**

At four stations randomly selected from the 15, the three sediment grabs were not composited; instead, these were submitted as individual replicate samples to provide information on within-station variability.

At two of the stations randomly selected from the 15, enough sediment was collected to permit the submission of blind duplicate ("split") samples for all analyses.

### **4.0 ANALYTICAL METHODS**

#### **4.1 Point Source (Effluent)**

Large volume samples were analyzed under contract to the MOE's Great Lakes Section by Mann Testing Laboratories of Mississauga, Ontario.



Each 18 litre sample was extracted for 48 minutes with 350 ml of dichloromethane (DCM) in an all-glass Goulden Large Sample Extractor<sup>R</sup>. When extraction was complete, the sample container was rinsed with two 80 ml aliquots of DCM and this was extracted as well. The extractor was rinsed with two 30 ml aliquots of DCM and both the combined extracts and the rinses were dried over Na<sub>2</sub>SO<sub>4</sub>. Iso-octane (2 ml) was added to this and the extract concentrated under N<sub>2</sub> to 1 ml by rotary evaporation at 25°C and 20 mm Hg. Cleanup was by passing the concentrate through a 60/80 mesh, 3%, deactivated Florisil column.

Surrogates used in spike recovery tests included decachlorobiphenyl (100 ng), d<sub>10</sub>-anthracene (200 ng) and d<sub>8</sub>-naphthalene (199 ng).

Detection and quantification of PCNs, PCBs/OCs and CBs was by gas chromatography (GC)/dual electron capture detector (ECD), using 30 m, 0.25 mm I.D. DB-5 and DB-17 columns.

Analysis for PAHs utilized a 60 m DB-5 capillary column, 0.25 mm I.D. and Varian Saturn GC/mass spectrometry (MS) system (Mann, 1990). PCN results were compared to the profiles for six Hallowax mixtures and three chlorinated naphthalene isomers.

#### **4.2 Water**

Owen Sound Harbour water samples were analyzed for calcium, chloride, suspended solids, dissolved organic carbon and conductivity according to documented Laboratory Services Branch methods (MOE, 1983 and updates).

Analysis for total PCNs in 1 litre samples was also based on documented methods for PCBs analysis (MOE, 1983), with the following minor modifications. To prevent PCNs from adhering to glassware during extraction, 20 drops of 50% H<sub>2</sub>SO<sub>4</sub> were added prior to extraction with DCM. Clean-up column elution solvent was changed to 40 ml of 25% DCM in hexane, concentrated to 2 ml prior to analysis. Detection and quantitation were by GC-ECD, compared to the Hallowax 1099 profile (MOE, 1990).

Large volume (18 litre) samples were analyzed by Mann Testing Laboratories, as described above for point sources.



### 4.3 Sediment

Surficial sediment samples and sewage sludge were analyzed by MOE's Laboratory Services Branch according to documented procedures for particle size, nutrients, trace metals, solvent extractables (oil and grease), PCBs and OCs, CBs and PAHs (MOE, 1983 and updates).

Analysis of these samples for total PCNs was based on documented methods for PCBs (MOE, 1983), with the following modifications: clean-up was on a 2.5 g equivalent aliquot; concentration was to 0.5 ml prior to analysis; and detection and quantification were by GC/mass selective detector (MSD), compared to the Halowax 1099 profile (MOE, 1990).

## 5.0 RESULTS AND DISCUSSION

The following sections focus on data for point source, water and sediment samples only. At the time of writing, benthic macroinvertebrate and caged mussel samples had not yet been submitted for analysis. The decision as to whether or not they will be analyzed will be made once a thorough analysis of data from this study and from others (sediment toxicity, young-of-the-year fish and sport fish) has been completed.

Field and laboratory quality assurance data for water and sediments are discussed in Appendices B and C, respectively.

### 5.1 Point Sources

Of the four discharges at which large volume samples were collected, PCNs were only found in the Goodyear effluent, at 13 ng/l. This is just above the method detection limit (MDL) of 10 ng/l. The PCN mixture most closely resembled Halowax 1099 (Table 2).

No PCBs were detected in any discharge samples; however, the alpha and gamma isomers of benzene hexachloride (BHC) were found at low concentrations (<0.1 to 2 ng/l) in samples from the Owen Sound WPCP, Kenny Drain and the 32nd St. E. storm sewer. These concentrations are similar to or below those reported for samples from other Ontario WPCP effluents (CAWPRC, 1987). However, similar low levels of alpha- and beta BHC were also found in a distilled water blank (Appendix B), indicating that the discharges sampled do not constitute major sources.



Table 2. Concentration of trace organics (ng/l) in Owen Sound Harbour point source discharges (large volume samples).

| Parameter                                         | MDL * | Source                              |                                           |                                         |                                      |
|---------------------------------------------------|-------|-------------------------------------|-------------------------------------------|-----------------------------------------|--------------------------------------|
|                                                   |       | Goodyear<br>final (GAC)<br>effluent | 32nd St. East<br>storm sewer<br>discharge | Kenny Drain<br>storm sewer<br>discharge | Owen Sound<br>WPCP final<br>effluent |
| <u>Polychlorinated Naphthalenes (PCNs):</u>       |       |                                     |                                           |                                         |                                      |
| 1-Chloronaphthalene                               | 20    | nd                                  | nd                                        | nd                                      | nd                                   |
| 2-Chloronaphthalene                               | 20    | nd                                  | nd                                        | nd                                      | nd                                   |
| Octachloronaphthalene                             | 10    | nd                                  | nd                                        | nd                                      | nd                                   |
| Halowax 1000                                      | 10    | nd                                  | nd                                        | nd                                      | nd                                   |
| Halowax 1001                                      | 10    | nd                                  | nd                                        | nd                                      | nd                                   |
| Halowax 1099                                      | 10    | 13                                  | nd                                        | nd                                      | nd                                   |
| Halowax 1013                                      | 10    | nd                                  | nd                                        | nd                                      | nd                                   |
| Halowax 1014                                      | 10    | nd                                  | nd                                        | nd                                      | nd                                   |
| Halowax 1051                                      | 10    | nd                                  | nd                                        | nd                                      | nd                                   |
| <u>PCBs/Organochlorine Pesticides (PCBs/OCs):</u> |       |                                     |                                           |                                         |                                      |
| Total PCBs                                        | 10.0  | nd                                  | nd                                        | nd                                      | nd                                   |
| Aldrin                                            | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Dieldrin                                          | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| alpha-BHC                                         | 0.1   | nd                                  | 0.2                                       | 0.4                                     | TR                                   |
| beta-BHC                                          | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| gamma-BHC (Lindane)                               | 0.1   | nd                                  | TR                                        | 0.1                                     | 2.0                                  |
| alpha-Chlordane                                   | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| gamma-Chlordane                                   | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| p,p-DDD                                           | 0.5   | nd                                  | nd                                        | nd                                      | nd                                   |
| p,p'-DDE                                          | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| o,p'-DDT                                          | 0.5   | nd                                  | nd                                        | nd                                      | nd                                   |
| p,p'-DDT                                          | 0.5   | nd                                  | nd                                        | nd                                      | nd                                   |
| Endrin                                            | 0.4   | nd                                  | nd                                        | nd                                      | nd                                   |
| alpha-Endosulphan                                 | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| beta-Endosulphan                                  | 0.4   | nd                                  | nd                                        | nd                                      | nd                                   |
| Endosulphan Sulphate                              | 0.4   | nd                                  | nd                                        | nd                                      | nd                                   |
| Heptachlor                                        | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Heptachlor epoxide                                | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Oxychlordane                                      | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| Methoxychlor (DMDT)                               | 0.4   | nd                                  | nd                                        | nd                                      | nd                                   |
| Mirex                                             | 0.5   | nd                                  | nd                                        | nd                                      | nd                                   |
| <u>Chlorobenzenes (CBs):</u>                      |       |                                     |                                           |                                         |                                      |
| Hexachlorobutadiene (HCBD)                        | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Hexachloroethane (HCE)                            | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Pentachlorobenzene (QCB)                          | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Hexachlorobenzene (HCB)                           | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 1,2,3,4-Tetrachlorobenzene (TeCB)                 | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 1,2,3,5-Tetrachlorobenzene                        | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 1,2,4,5-Tetrachlorobenzene                        | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 1,2,4-Trichlorobenzene                            | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 1,2,3-Trichlorobenzene (TCB)                      | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| 1,3,5-Trichlorobenzene                            | 0.2   | nd                                  | nd                                        | nd                                      | nd                                   |
| 2,3,6-Trichlorotoluene (TCT)                      | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 2,4,5-Trichlorotoluene                            | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| 2,6,a-Trichlorotoluene                            | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |
| Octachlorostyrene (OCS)                           | 0.1   | nd                                  | nd                                        | nd                                      | nd                                   |

Table 2. Concentration of trace organics (ng/l) in Owen Sound Harbour point source discharges (large volume samples). (continued)

| Polycyclic Aromatic Hydrocarbons (PAHs): |   |    |    |    |    |    |
|------------------------------------------|---|----|----|----|----|----|
| Anthracene                               | 1 | nd | nd | nd | nd | nd |
| Benzo(a)Anthracene                       | 1 | nd | nd | nd | nd | nd |
| Benzo(b)Fluoranthene                     | 3 | nd | nd | nd | nd | nd |
| Benzo(k)Fluoranthene                     | 3 | nd | nd | nd | nd | nd |
| Benzo(g,h,i)Perylene                     | 3 | nd | nd | nd | nd | nd |
| Benzo(a)Pyrene                           | 3 | nd | nd | nd | nd | nd |
| Chrysene                                 | 1 | nd | nd | nd | nd | nd |
| Coronene                                 | 3 | nd | nd | nd | nd | nd |
| Dibenzo(a,h)Anthracene                   | 3 | nd | nd | nd | nd | nd |
| Dimethyl Benzo(a)Anthracene              | 3 | nd | nd | nd | nd | nd |
| Fluoranthene                             | 1 | 1  | 2  | nd | nd | nd |
| Indeno(1,2,3-cd)Pyrene                   | 3 | nd | nd | nd | nd | nd |
| Phenanthrene                             | 1 | 1  | 2  | nd | nd | nd |
| Perylene                                 | 3 | nd | nd | nd | nd | nd |
| Pyrene                                   | 1 | 2  | 2  | nd | nd | nd |

NOTES: nd = not detected.

TR = trace amount detected.

MDL = method detection limit.

\* MDLs for Kenny Drain (PAHs only) and Owen Sound WPCP (all parameters) were ten times higher due to very high hydrocarbon background.



The PAH compounds fluoranthene, phenanthrene and pyrene were found at concentrations of 1 to 2 ng/l in the Goodyear effluent and 32nd St. E. storm sewer samples (Table 2). These levels are about an order of magnitude or more lower than the mean concentrations reported for Metro Toronto WPCP effluent samples (CAWPRC, 1987).

Unfortunately, a high hydrocarbon background in the Kenny Drain and Owen Sound WPCP samples resulted in a 10-fold increase in the method detection level (MDL) for PAHs (and of PCBs/OCs and CBs in the latter as well). This may account for the non-detection of PAHs in these two discharges.

## **5.2 Water**

### **Conventional Parameters**

Direction of water flow along the eastern nearshore of Owen Sound Harbour was northward during the survey (i.e., from SW to NE). Except for periods with strong northerly winds, this is the predominant direction of flow (J. Westwood, MOE, pers. comm., 1990).

Data on the basic physical and chemical characteristics of Owen Sound Harbour water during the survey are summarized in Tables 3 and 4.

Water temperature varied over a range of about 3°C, with temperatures of 10.4 to 11.7°C recorded during the first three days of the survey (October 17-18). By the 4th day, however, the change in weather systems, with winds shifting to the north and north-west, resulted in the influx of cooler water, and water temperatures dropped to 8.4 to 9.1°C. Despite this shift, there was no clear evidence of any thermal impact by the Goodyear discharge. Also, there was little difference between surface and bottom water temperatures (Table 3).

Dissolved oxygen levels were high, ranging between 10.20 and 12.55 mg O<sub>2</sub>/l, with slightly lower concentrations (i.e., <1 mg O<sub>2</sub>/l lower) in bottom waters than at the surface. These concentrations were, nevertheless, well above the minimum of 54% saturation required for the protection of cold water biota (MOE, 1984).

Table 3. Owen Sound Harbour field water quality data.

| Station                  |                        |                |               | Parameter              |        |              |        |            |        |                          |        |
|--------------------------|------------------------|----------------|---------------|------------------------|--------|--------------|--------|------------|--------|--------------------------|--------|
| Number                   | Distance from shore, m | Water depth, m | Sampling date | Temperature, °C        |        | Oxygen, mg/L |        | pH         |        | field Cond., µs/cm @25°C |        |
|                          |                        |                |               | surface                | bottom | surface      | bottom | surface    | bottom | surface                  | bottom |
| 45                       | 400                    | 2.80           | Oct. 19       | 9.3                    | 9.3    | 10.80        | 10.50  | -          | -      | 200                      | 200    |
| 43                       | 100                    | 1.70           | Oct. 19       | 8.8                    | 8.8    | 11.10        | 10.80  | -          | -      | 201                      | 201    |
| 44                       | 300                    | 1.50           | Oct. 18       | 8.9                    | 8.9    | 12.55        | 12.50  | -          | -      | 200                      | 200    |
| 40                       | 60                     | 2.00           | Oct. 19       | 8.4                    | 8.5    | 11.15        | 10.55  | -          | -      | 201                      | 202    |
| 41                       | 175                    | 1.50           | Oct. 17       | 11.5                   | 11.7   | 11.20        | 10.55  | 7.33       | 7.32   | 200                      | 200    |
| 42                       | 300                    | 1.90           | Oct. 19       | 9.1                    | 9.1    | 10.70        | 10.55  | -          | -      | 201                      | 201    |
| 39                       | 40                     | 2.00           | Oct. 18       | 11.4                   | 11.1   | 11.10        | 11.05  | -          | -      | 292                      | 282    |
| 38                       | 100                    | 1.50           | Oct. 17       | 10.4                   | 10.4   | 11.15        | 11.15  | 7.95       | 7.80   | 241                      | 241    |
| 37                       | 195                    | 1.80           | Oct. 16       | 11.1                   | 11.0   | 11.40        | 11.35  | 7.22       | 7.57   | 244                      | 246    |
| 36                       | 320                    | 7.50           | Oct. 16       | 11.1                   | 11.0   | 11.25        | 11.15  | 8.12       | 6.87   | 194                      | 195    |
| 46                       | 50                     | 2.20           | Oct. 18       | 11.5                   | 11.5   | 11.05        | 10.35  | -          | -      | 306                      | 304    |
| 47                       | 150                    | 1.50           | Oct. 19       | 8.7                    | 8.8    | 10.74        | 10.20  | -          | -      | 202                      | 202    |
| Aquatic Life Objective * |                        |                |               | < 30°C or < 10°C incr. |        | > 54% sat'n. |        | 6.5 to 8.5 |        | NA                       |        |

NOTES: Cond. = conductivity.

\* = MOE (1984).

incr. = less than 10°C increase above natural ambient water temperature at edge of mixing zone.

satur'n. = saturation between 0 and 15°C, for the protection of cold water biota.

NA = not available.



Due to malfunction of the pH meter, data were only obtained for the first four stations sampled (Table 3). Fortunately, these were within the immediate area of the Goodyear discharge (see Figure 2). Although pH varied somewhat, ranging between 6.87 and 8.12, there were no clear trends with respect to depth or distance. Values were within the pH range of 6.5 to 8.5 required for the protection of aquatic life and for recreational purposes (MOE, 1984).

Although conductivity measured in the field (Table 3) was slightly higher (by 2-16 us/cm) than that measured in water samples submitted for laboratory analysis (Table 4), the two data sets concurred spatially. There was little difference between surface and bottom waters; however, a distinct spatial pattern was observed. Conductivity was highest closest to shore and upstream (south-west) of the Goodyear discharge, in the vicinity of the 32nd Street East storm sewer (295-306 us/cm). At 40 m offshore from the Goodyear discharge (about 100 m north-east of the storm sewer), conductivity was still elevated, at 270-292 us/cm. Thereafter, however, conductivity decreased rapidly, both with increases in distance north-east of the Goodyear outfall, as well as with distance offshore. For example, at a station 100 m downstream of Goodyear and 60 m offshore, conductivity was 194-202 us/cm, very similar to that at 320 m from the discharge (191-194 us/cm).

The ranges in the concentrations of calcium, chloride and dissolved organic carbon were 26.46 to 50.00 mg/l, 3.40 to 10.00 mg/l and 1.4 to 3.7 mg/l, respectively (Table 4). To a large degree, these parameters exhibited a spatial and temporal variation similar to that observed for conductivity.

Suspended solids concentrations were more variable than the foregoing parameters, ranging from approximately 0 to 30.5 mg/L. Field split sample and replicate data showed that up to 35% of this spatial variability is due to problems related to obtaining representative samples. Nevertheless, concentrations on October 19, and/or at stations closest to shore, were probably significantly above those at other stations (Table 4).



The high dissolved solids (conductivity) and suspended solids concentrations in the nearshore zone were mainly the result of discharges south-west of the Goodyear plant, and not the Goodyear effluent. The former include the Owen Sound WPCP, a number of storm sewers and an urban drain (Figure 2). In fact, rainfall on October 17 and 18 (Appendix A, Table A-3) resulted in heavy flows from the latter three discharges, and a noticeable nearshore turbidity plume which largely began at the Kenny Drain, about 0.75 km south-west of Goodyear. Increases in suspended solids concentrations in samples obtained on October 19 in the nearshore relative to other samples were above the maximum allowable 10% increase in turbidity (MOE, 1984).

### Organics

Analysis of 1 litre water samples from the 12 nearshore stations for total PCNs used Halowax 1099 as the standard. No PCNs were detected in any of the samples at a MDL of 20 ng/l (Table 4).

Large volume (18 litre) samples from six of the above stations in the immediate vicinity of the Goodyear discharge also did not contain any PCNs at a MDL of 10 ng/l (Table 5). In addition to Halowax 1099, analysis was also performed for Halowax 1000, Halowax 1001, Halowax 1013, Halowax 1014, Halowax 1051, two chloronaphthalene isomers and octachloronaphthalene.

PCBs were not detected in any of the large volume samples. Of the OCs, only the alpha- and gamma-BHC isomers were found; concentrations at the six stations ranged from 0.6 to 1.5 ng/l and 0.3 to 0.5 ng/l, respectively (Table 5). Similar concentrations were found in a distilled water blank (Appendix B). The concentrations of lindane (gamma-BHC) were well below the 10 ng/l objective for the protection of aquatic life (MOE, 1984 GLWQA, 1987). Both BHC isomers seem to be ubiquitous in Great Lakes waters; however, their concentrations in Owen Sound Harbour samples were somewhat lower than the mean levels reported for Lake Huron and Georgian Bay: 5.9 and 5.1 ng/l for alpha-BHC; 0.8 and 0.7 ng/l for gamma-BHC (IJC, 1989).

Of the CBs, only hexachloroethane (HCE) was found at trace levels (<0.1 ng/l) at stations 38, 40 and 43 (Table 5). A trace of HCE was also detected in a distilled water blank (Appendix B).



Table 4. Concentration of polychlorinated naphthalenes and conventional parameters in Owen Sound Harbour water samples.

| Station                  |                     |               | Parameter        |        |                                          |        |               |        |                |        |           |        |                |        |
|--------------------------|---------------------|---------------|------------------|--------|------------------------------------------|--------|---------------|--------|----------------|--------|-----------|--------|----------------|--------|
| Number                   | Dist. from shore, m | Sampling date | Total PCNs, ng/l |        | lab. Cond., $\mu\text{S}/\text{cm}$ @25° |        | Calcium, mg/l |        | Chloride, mg/l |        | DOC, mg/l |        | S.Solids, mg/l |        |
|                          |                     |               | surface          | bottom | surface                                  | bottom | surface       | bottom | surface        | bottom | surface   | bottom | surface        | bottom |
| 45                       | 400                 | Oct. 19       | <20<W            | <20<W  | 193                                      | 193    | 29.35         | 27.70  | 5.40           | 5.10   | 1.4       | 1.5    | 3.1            | 3.4    |
| 43                       | 100                 | Oct. 19       | <20<W            | <20<W  | 194                                      | 200    | 28.00         | 30.50  | 5.10           | 5.00   | 1.5       | 1.6    | 18.2           | 22.6   |
| 44                       | 300                 | Oct. 18       | <20<W            | <20<W  | 192                                      | 192    | 26.72         | 26.81  | 3.40           | 4.60   | 1.5       | 1.6    | 0.5<W          | <0.5<W |
| 40                       | 60                  | Oct. 19       | <20<W            | <20<W  | 195                                      | 194    | 28.80         | 28.30  | 4.70           | 5.90   | 1.4       | 1.4    | 22.5           | 30.5   |
| 41                       | 175                 | Oct. 17       | <20<W            | <20<W  | 192                                      | 192    | 26.46         | 26.62  | 4.95           | 4.90   | 1.6       | 1.7    | 3.0            | 1.7<T  |
| 42                       | 300                 | Oct. 19       | <20<W            | <20<W  | 193                                      | 194    | 50.00         | 47.30  | 5.00           | 4.90   | 1.5       | 1.7    | 5.1            | 1.7<T  |
| 39                       | 40                  | Oct. 18       | <20<W            | <20<W  | 283                                      | 270    | 39.17         | 35.70  | 9.30           | 8.60   | 3.2       | 3.4    | 3.5            | 2.2<T  |
| 38                       | 100                 | Oct. 17       | <20<W            | <20<W  | 239                                      | 226    | 32.82         | 31.33  | 8.20           | 7.60   | 2.9       | 2.3    | 2.4<T          | 2.0<T  |
| 37                       | 195                 | Oct. 16       | <20<W            | <20<W  | 239                                      | 241    | 33.43         | 33.71  | 7.60           | 7.80   | 3.3       | 3.0    | 4.3            | 1.5<T  |
| 36                       | 320                 | Oct. 16       | <20<W            | <20<W  | 191                                      | 191    | 26.84         | 27.04  | 4.90           | 4.90   | 1.7       | 1.5    | 1.8<T          | 1.2<T  |
| 46                       | 50                  | Oct. 18       | <20<W            | <20<W  | 297                                      | 295    | 41.47         | 41.01  | 10.00          | 8.70   | 3.7       | 3.7    | 4.4            | 2.9    |
| 47                       | 150                 | Oct. 19       | <20<W            | <20<W  | 195                                      | 194    | 39.90         | 38.50  | 5.00           | 4.90   | 1.7       | 2.0    | 21.4           | 21.5   |
| Method Detection Limit   |                     |               | 20 ng/l          |        | 0.2 $\mu\text{S}/\text{cm}$              |        | 0.1 mg/l      |        | 0.2 mg/l       |        | 1 mg/l    |        | 0.5 mg/l       |        |
| Aquatic Life Objective * |                     |               | NA               |        | NA                                       |        | NA            |        | NA             |        | NA        |        | < 10 % incr.   |        |

NOTES: <T = a measurable trace amount; interpret with caution.  
 <W = no measurable response (zero); less than reported value.  
 Cond. = Conductivity.  
 DOC = Dissolved Organic Carbon.  
 S.Solids = Suspended Solids.  
 incr. = less than 10 % increase in Secchi disc reading.  
 \* = MOE (1984).  
 NA = not available.



Of the 16 PAH compounds analyzed for in the large volume samples, only four were detected. (The high hydrocarbon background in the sample from station 46 resulted in 10-fold higher detection limits for PAHs, resulting in "non-detects" for all compounds.) Fluoranthene, phenanthrene and pyrene were, however, detected at five of the six stations, at concentrations of 2 to 6 ng/l, 1 to 2 ng/l and 2 to 12 ng/l, respectively (Table 5). Peak concentrations of these compounds were found at station 38, 100 m from the Goodyear discharge (Figure 2). Benzo(a)anthracene was also found, but only at station 39, 40 m from the Goodyear discharge.

There are currently no aquatic life objectives for PAH compounds in water to compare the Owen Sound Harbour data with. Fluoranthene, phenanthrene and pyrene concentrations in Owen Sound Harbour were, however, somewhat lower than the mean concentrations for the Great Lakes (i.e., 15, 24 and 14 ng/l, respectively - IJC 1983).

Although nearshore water samples were collected a day prior to the point source samples, the detection of higher concentrations of fluoranthene, phenanthrene and pyrene near the Goodyear discharge, combined with their detection (albeit at lower levels) in the Goodyear final effluent and the 32nd St. E. storm sewer discharge suggest that these may be sources of PAHs. Furthermore, the presence of fluoranthene and pyrene is indicative of high temperature combustion of fossil fuels as the major source of PAHs (Helfrich & Armstrong, 1986).

### 5.3 Sediment

#### Physical Characteristics

The eastern shore of Owen Sound Harbour in the study area is characterized by a 300-400 m wide band of shallow water, 2 m or less in depth. Further offshore, water depth increases rapidly to  $\geq 20$  m (Figure 1), eventually forming the Owen Sound Trough, a depositional zone extending northward into Georgian Bay (IJC, 1977).



Table 5. Concentration of trace organics (ng/l) in Owen Sound Harbour large volume water samples.

| Parameter                                         | MDL * | Aquatic **<br>Life<br>Objective | Station |     |     |     |     |     |    |
|---------------------------------------------------|-------|---------------------------------|---------|-----|-----|-----|-----|-----|----|
|                                                   |       |                                 | 39      | 38  | 40  | 43  | 46  | 45  |    |
| <b>Polychlorinated Naphthalenes (PCNs):</b>       |       |                                 |         |     |     |     |     |     |    |
| 1-Chloronaphthalene                               | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 2-Chloronaphthalene                               | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Octachloronaphthalene                             | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Halowax 1000                                      | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Halowax 1001                                      | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Halowax 1099                                      | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Halowax 1013                                      | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Halowax 1014                                      | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Halowax 1051                                      | 10    | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| <b>PCBs/Organochlorine Pesticides (PCBs/OCs):</b> |       |                                 |         |     |     |     |     |     |    |
| Total PCBs                                        | 10    | 1                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Aldrin                                            | 0.1   | }                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Dieldrin                                          | 0.2   |                                 | nd      | nd  | nd  | nd  | nd  | nd  |    |
| alpha-BHC                                         | 0.1   | -                               | 0.6     | 1.1 | 1.5 | 1.2 | 1.0 | 1.1 |    |
| beta-BHC                                          | 0.1   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| gamma-BHC (Lindane)                               | 0.1   | 10                              | 0.2     | 0.5 | 0.4 | 0.4 | 0.3 | 0.3 |    |
| alpha-Chlordane                                   | 0.2   | }                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| gamma-Chlordane                                   | 0.2   |                                 | -       | nd  | nd  | nd  | nd  | nd  | nd |
| p,p'-DDD                                          | 0.5   | }                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| p,p'-DDE                                          | 0.1   |                                 | 3       | nd  | nd  | nd  | nd  | nd  | nd |
| o,p'-DDT                                          | 0.5   |                                 | nd      | nd  | nd  | nd  | nd  | nd  | nd |
| p,p'-DDT                                          | 0.5   | }                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Endrin                                            | 0.4   |                                 | 2       | nd  | nd  | nd  | nd  | nd  | nd |
| alpha-Endosulphan                                 | 0.2   | }                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| beta-Endosulphan                                  | 0.4   |                                 | 3       | nd  | nd  | nd  | nd  | nd  | nd |
| Endosulphan Sulphate                              | 0.4   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Heptachlor                                        | 0.1   | 1                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Heptachlor epoxide                                | 0.1   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Oxychlordane                                      | 0.2   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Methoxychlor (DNMT)                               | 0.4   | 40                              | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Mirex                                             | 0.5   | 1                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| <b>Chlorobenzenes (CBs):</b>                      |       |                                 |         |     |     |     |     |     |    |
| Hexachlorobutadiene (HCBD)                        | 0.1   | 100                             | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Hexachloroethane (HCE)                            | 0.1   | -                               | nd      | TR  | TR  | TR  | nd  | nd  |    |
| Pentachlorobenzene (QCB)                          | 0.1   | 30                              | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Hexachlorobenzene (HCB)                           | 0.1   | 6.5                             | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 1,2,3,4-Tetrachlorobenzene (TeCB)                 | 0.1   | 10                              | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 1,2,3,5-Tetrachlorobenzene                        | 0.1   | 10                              | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 1,2,4,5-Tetrachlorobenzene                        | 0.1   | 15                              | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 1,2,3-Trichlorobenzene (TCB)                      | 0.1   | 900                             | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 1,2,4-Trichlorobenzene                            | 0.2   | 500                             | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 1,3,5-Trichlorobenzene                            | 0.2   | 650                             | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 2,3,6-Trichlorotoluene (TCT)                      | 0.1   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 2,4,5-Trichlorotoluene                            | 0.1   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| 2,6-a-Trichlorotoluene                            | 0.1   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |
| Octachlorostyrene (OCS)                           | 0.1   | -                               | nd      | nd  | nd  | nd  | nd  | nd  |    |

Table 5. Concentration of trace organics (ng/l) in Owen Sound Harbour large volume water samples. (continued)

| Polycyclic Aromatic Hydrocarbons (PAHs): |   |   |     |      |     |     |    |     |     |
|------------------------------------------|---|---|-----|------|-----|-----|----|-----|-----|
| Anthracene                               | 1 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Benzo(a)Anthracene                       | 1 | - | 2.0 | nd   | nd  | nd  | nd | nd  | nd  |
| Benzo(b)Fluoranthene                     | 3 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Benzo(k)Fluoranthene                     | 3 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Benzo(g,h,i)Perylene                     | 3 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Benzo(a)Pyrene                           | 1 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Chrysene                                 | 3 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Coronene                                 | 3 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Dibenzo(a,h)Anthracene                   | 3 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Dimethyl Benzo(a)Anthracene              | 1 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Fluoranthene                             | 3 | - | 2.0 | 6.0  | 2.0 | 2.0 | nd | 2.0 | 2.0 |
| Indeno(1,2,3-cd)Pyrene                   | 1 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Phenanthrene                             | 3 | - | 2.0 | 1.0  | 1.0 | 2.0 | nd | 1.0 | 1.0 |
| Perylene                                 | 1 | - | nd  | nd   | nd  | nd  | nd | nd  | nd  |
| Pyrene                                   | 4 | - | 2.0 | 12.0 | 4.0 | 4.0 | nd | 3.0 | 3.0 |

NOTES: nd = not detected.

TR = trace amount.

MDL = method detection limit.

\* MDL for PAHs at station 46 was ten times that indicated due to very high hydrocarbon background.

\*\* = MOE (1984) and IJC (1978).

"-" = not available.



Good water clarity on October 16 allowed visual observations of the bottom to be made along transects running out from shore. These indicated that surficial sediments in the survey area are largely composed of clean, silty sand, with patches of the macroalga Chara, and occasional growths of the macrophytes Myriophyllum and Potamogeton. These observations were similar to those of previous MOE studies (MOE, 1980; Bio-Environmental Services, 1980). The occasional freshwater mussel was also observed.

Closer to shore, sediment gives way to cobble, boulders, and finally, sandstone bedrock that increases in width as one moves further north. For example, at the Goodyear discharge, this stone bottom extended about 30 to 40 m out from shore, which dictated the closest-to-shore sampling station (stn. 38). At 100 m north-east of the discharge, the outcrop extended about 60 m offshore, while at 300 m north-east it was present as far as 100 m offshore.

In deeper waters, such as near the Owen Sound Water Treatment Plant intake (i.e., >10 m depth), the sediments are a fine, gray silt devoid of plant growth.

#### **Nutrients and Trace Metals**

Surficial sediments contained relatively low concentrations of nutrients and trace metals, and for the most part, spatial (station-to-station) variability was also low. With the exception of loss on ignition (LOI), total organic carbon (TOC), copper and lead, concentrations of contaminants varied less than 3-fold between minimum and maximum (Table 7).

Concentrations of TOC and LOI, the latter also a measure of organic carbon, were somewhat more variable in sediments, ranging from 0 to 14.07 g/kg and from 4.4 to 22.5 g/kg, respectively. The highest levels of these parameters were found at station 46, just north of the 32nd St. E. storm sewer outfall (Figure 2). The highest concentration of total Kjeldahl nitrogen (TKN) was also found at this station (1.03 g/kg - Table 7).



Table 6. Physical characteristics of Owen Sound Harbour surficial sediments.

| Station                |                        |                |               | Sediment                                           |                                   |                       |                        |
|------------------------|------------------------|----------------|---------------|----------------------------------------------------|-----------------------------------|-----------------------|------------------------|
| Number                 | Distance from shore, m | Water depth, m | Sampling date | Visual Description                                 | Particle Size Distribution (%)    |                       |                        |
|                        |                        |                |               |                                                    | 2000 to 1000µm<br>(v.coarse sand) | 999 to 62µm<br>(sand) | <62µm<br>(silt & clay) |
| 45                     | 400                    | 2.90           | Oct.19        | silty sand.                                        | 0.00                              | 13.90                 | 86.00                  |
| 43                     | 100                    | 1.60           | Oct.19        | sandy silt.                                        | 3.00                              | 32.50                 | 67.01                  |
| 44                     | 300                    | 1.50           | Oct.18        | brown and some black sand; very little silt.       | 0.09                              | 94.20                 | 6.73                   |
| 40                     | 60                     | 2.00           | Oct.19        | silty sand over clay; macrophytes.                 | 0.07                              | 77.25                 | 21.16                  |
| 41                     | 175                    | 1.50           | Oct.17        | silty sand (brown/black sand); detritus.           | 0.05                              | 85.23                 | 14.51                  |
| 42                     | 300                    | 1.90           | Oct.19        | sand; trace of silt.                               | 0.10                              | 87.00                 | 12.92                  |
| 39                     | 40                     | 2.00           | Oct.18        | sand and clay; macrophytes.                        | 0.20                              | 58.00                 | 41.53                  |
| 38                     | 100                    | 1.50           | Oct.17        | brown sand over black sand; clay; oily odour.      | 0.10                              | 86.03                 | 13.65                  |
| 37                     | 195                    | 1.80           | Oct.16        | silty sand.                                        | 7.00                              | 85.70                 | 14.18                  |
| 36                     | 320                    | 7.50           | Oct.16        | silty sand; macrophytes.                           | 0.10                              | 72.70                 | 27.12                  |
| 46                     | 50                     | 2.20           | Oct.18        | silty sand over clay; stones; macrophytes.         | 0.13                              | 47.23                 | 49.69                  |
| 47                     | 150                    | 1.60           | Oct.19        | silty sand; macrophytes.                           | 0.03                              | 85.16                 | 14.59                  |
| 48                     | 50                     | 2.00           | Oct.19        | clay, some sand.                                   | 0.10                              | 25.40                 | 74.03                  |
| 49                     | 50                     | 1.60           | Oct.19        | sand over clay.                                    | 0.10                              | 36.90                 | 62.61                  |
| 50                     | 880                    | 14.20          | Oct.19        | silt.                                              | 0.10                              | 42.70                 | 56.84                  |
| 2                      | -50                    | -              | Oct.19        | black, organic; strong sewage odour (WPCP sludge). | NA                                | NA                    | NA                     |
| Method Detection Limit |                        |                |               | -                                                  | 0.10                              | 0.10                  | 0.10                   |

NOTES: NA = not available.



Table 7. Concentrations of nutrients and trace metals in Owen Sound Harbour surficial sediments.

| Station           |                     | Parameter |              |              |             |               |               |                |              |            |            |               |              |            |  |
|-------------------|---------------------|-----------|--------------|--------------|-------------|---------------|---------------|----------------|--------------|------------|------------|---------------|--------------|------------|--|
| Number            | Dist. from shore, m | LOI g/kg  | TOC g/kg     | Phosph. g/kg | TKN g/kg    | Arsenic mg/kg | Cadmium mg/kg | Chromium mg/kg | Copper mg/kg | Iron mg/kg | Lead mg/kg | Mercury mg/kg | Nickel mg/kg | Zinc mg/kg |  |
| 45                | 400                 | 9.0       | 2.60         | 0.43         | <u>0.73</u> | 2.00          | 0.10<T        | 9.20           | 9.60         | 8900       | 1.00<T     | 0.02<T        | 10.00        | 19.00      |  |
| 43                | 100                 | 13.0      | 4.80         | <u>0.59</u>  | <u>0.62</u> | 2.00          | 0.21<T        | 15.00          | 15.00        | 14000      | 1.20<T     | <0.01<W       | 15.00        | 26.00      |  |
| 44                | 300                 | 4.4       | <0.20<W      | <u>0.74</u>  | 0.36        | 1.25          | 0.39          | 16.97          | 6.30         | 20976      | <1.00<W    | <0.01<W       | 8.80         | 21.80      |  |
| 40                | 60                  | 20.1      | 4.58         | <u>0.71</u>  | <u>0.73</u> | 1.77          | 0.42          | 13.28          | 11.32        | 12657      | 3.08<T     | <0.01<W       | 11.00        | 25.33      |  |
| 41                | 175                 | 7.9       | 0.70         | <u>0.56</u>  | <u>0.34</u> | 1.50          | 0.14<T        | 11.00          | 9.15         | 11489      | <1.00<W    | <0.01<W       | 9.60         | 18.00      |  |
| 42                | 300                 | 5.0       | 3.50         | <u>0.57</u>  | 0.44        | 1.60          | <0.05<W       | 9.30           | 4.90         | 9200       | 1.50<T     | <0.01<W       | 10.00        | 22.00      |  |
| 39                | 40                  | 15.0      | 7.70         | <u>0.64</u>  | <u>0.61</u> | 1.90          | 0.23<T        | 13.00          | 16.00        | 13000      | 3.60<T     | <0.01<W       | 13.00        | 27.00      |  |
| 38                | 100                 | 10.4      | 3.04         | <u>0.65</u>  | 0.53        | 2.07          | 0.31          | 12.33          | 9.01         | 13658      | <1.00<W    | <0.01<W       | 10.18        | 19.98      |  |
| 37                | 195                 | 8.9       | 1.90         | <u>0.56</u>  | 0.45        | 1.60          | <0.05<W       | 9.20           | 9.90         | 8500       | <1.00<W    | <0.01<W       | 9.20         | 19.00      |  |
| 36                | 320                 | 14.0      | 5.80         | 0.55         | <u>0.77</u> | 2.30          | 0.18<T        | 11.00          | 11.00        | 11000      | 1.20<T     | <0.01<W       | 13.00        | 26.00      |  |
| 46                | 50                  | 22.5      | <u>14.07</u> | <u>0.64</u>  | <u>1.03</u> | 2.53          | 0.46          | 15.00          | <u>16.64</u> | 13658      | 2.13<T     | <0.01<W       | 15.00        | 31.28      |  |
| 47                | 150                 | 8.8       | 4.71         | 0.52         | 0.60        | 2.00          | 0.25<T        | 9.47           | <u>10.97</u> | 8064       | 1.75<T     | <0.01<W       | 10.15        | 20.30      |  |
| 48                | 50                  | 18.0      | 6.00         | <u>0.62</u>  | 0.56        | 2.60          | 0.33          | 17.00          | <u>20.00</u> | 15000      | 4.00<T     | 0.02<T        | <u>18.00</u> | 28.00      |  |
| 49                | 50                  | 13.0      | 0.81<T       | <u>0.63</u>  | <u>0.65</u> | 2.60          | 0.28          | 16.00          | <u>19.00</u> | 12000      | <1.00<W    | <0.01<W       | 16.00        | 27.00      |  |
| 50                | 880                 | 22.0      | 10.00        | <u>0.65</u>  | <u>0.87</u> | 2.70          | 0.56          | 16.00          | <u>21.00</u> | 14000      | 9.70       | 0.03<T        | <u>18.00</u> | 43.00      |  |
| 2                 | -50                 | -         | -            | -            | -           | -             | <0.01<W       | 12.00          | <u>79.00</u> | 13780      | 14.00      | <u>0.23</u>   | <0.05<W      | 36.00      |  |
| MDL               |                     | 5.0       | 0.20         | 0.02         | 0.10        | 0.20          | 0.05          | 2.00           | 1.00         | 20         | 1.00       | 0.01          | 1.00         | 1.00       |  |
| Background *      |                     | NA        | NA           | NA           | NA          | 4.20          | 1.10          | 31.00          | 25.00        | 31200      | 23.00      | 0.10          | 31.00        | 65.00      |  |
| Dredge Guidel. ** | 60.0                | NA        | NA           | 1.00         | 2.00        | 8.00          | 1.00          | 25.00          | 25.00        | 10000      | 50.00      | 0.30          | 25.00        | 100.00     |  |
| LOEL ***          |                     | NA        | 10.00        | 0.55         | 0.60        | 6.00          | 0.60          | 26.00          | 16.00        | 20000      | 31.00      | 0.20          | 16.00        | 120.00     |  |

NOTES: LOI = loss on ignition.

TOC = total organic carbon.

TKN = total Kjeldahl nitrogen.

&lt;T = a measurable trace amount; interpret with caution.

&lt;W = no measurable response (zero): &lt; reported value.

MDL = method detection limit.

\* = background or pre-colonial concentration for Great Lakes sediments (Hart et al., 1988).

\*\* = concentration below which disposal of dredged material in open water is permitted (Persaud &amp; Wilkins, 1976).

\*\*\* = "lowest effect level" of contamination that can be tolerated by the majority of benthic organisms (Persaud et al., 1990).

Underlined values exceed the lower of \*\* or \*\*\*.



Copper and lead concentrations ranged from 6.30 to 21.00 mg/kg and from 0 to 9.70 mg/kg, respectively, with the highest levels being recorded in the finer sediments at station 50, near the Owen Sound Water Treatment Plant intake. Nevertheless, trace metal concentrations in all nearshore sediment samples were below the mean levels for non-depositional Georgian Bay and North Channel sediments (IJC, 1977). In fact, they were within the range considered to be "background" (i.e., pre-colonial) for the Great Lakes (Hart et al., 1988 and Table 7).

Trace metal concentrations also did not exceed the respective MOE guidelines for the open-water disposal of dredged material (Table 7).

If sediment concentrations are compared to the recently-proposed (draft) "lowest effect level (LOEL)" guidelines, however, then levels of phosphorus and TKN at more than half of the stations were slightly above the levels (0.55 g/kg and 0.60 g/kg, respectively) that could be tolerated by the majority of benthic organisms (Table 7).

Copper and nickel concentrations were also slightly above the proposed lowest effect level of 16 mg/kg at nearshore stations south-west (upstream) of the Goodyear plant (stations 46, 48, 49 and 50). It is perhaps noteworthy that these stations are near storm water discharges (stations 46, 48 and 49), as well as downstream of the Owen Sound WPCP discharge (e.g., station 50). Sediments from these stations contained somewhat higher proportions of the very small diameter silt and clay particles than many of the other stations. These nearshore stations also tended to have slightly higher sediment concentrations of arsenic, chromium, cadmium, iron and zinc (Table 7).

Concentrations of many of the trace metals, particularly cadmium, chromium, copper, lead, nickel and zinc, were also slightly higher at stations closer to shore than those further offshore, and this may be related both to the greater proportions of silt and clay particles as well as to the higher organic carbon content (Tables 6 and 7).



Table 8. Concentration of trace organics in Owen Sound Harbour surficial sediments.

| Station             |                        | Parameter                  |                                  |                  |                                   |                         |                                 |
|---------------------|------------------------|----------------------------|----------------------------------|------------------|-----------------------------------|-------------------------|---------------------------------|
| Number              | Distance from shore, m | Solvent Extractables mg/kg | Total PCNs as Halowax 1099 ug/kg | Total PCBs ug/kg | Organochlorine Pesticides * ug/kg | Chloro-benzenes * ug/kg | Polycyclic Aromatic HCs * ug/kg |
| 45                  | 400                    | 289                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 43                  | 100                    | 214                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 44                  | 300                    | 120                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 40                  | 60                     | 273                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 41                  | 175                    | 248                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 42                  | 300                    | 205                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 39                  | 40                     | 278                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 38                  | 100                    | 233                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 37                  | 195                    | 245                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 36                  | 320                    | 283                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 46                  | 50                     | 498                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 47                  | 150                    | 204                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 48                  | 50                     | 69                         | nd                               | nd               | nd                                | nd                      | nd                              |
| 49                  | 50                     | 121                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 50                  | 880                    | 208                        | nd                               | nd               | nd                                | nd                      | nd                              |
| 2                   | -50                    | <u>100000</u>              | nd                               | nd               | nd                                | nd                      | nd                              |
| MDL                 |                        | 1                          | 20                               | 20               | 1 to 5                            | 1 to 2                  | 10 to 70                        |
| Dredge Guideline ** |                        | 1500                       | NA                               | 50               | NA                                | NA                      | 1000 [B(a)P]                    |
| LOEL ***            |                        | NA                         | NA                               | 70               | 2 to 8                            | 20 [HCB]                | 2000 [ $\Sigma$ PAHs]           |

NOTES: HCs = hydrocarbons.

B(a)P = benzo(a)pyrene.

HCB = hexachlorobenzene.

\* = See Table 1 for compounds.

\*\* = concentration below which disposal of dredged material in open water is permitted (Persaud & Wilkins, 1976).

\*\*\* = "lowest effect level" of contamination that can be tolerated by the majority of benthic organisms (Persaud et al., 1990).

Underlined values exceed the lower of \*\* or \*\*\*.

NA = not available.



Due to the nature of the sample, sewage sludge from the Owen Sound WPCP (station 2-3) could only be analyzed for heavy metals. With the exception of slightly higher concentrations of copper (79 mg/kg), lead (14 mg/kg) and mercury (0.23 mg/kg) in the sludge, metal concentrations were similar to, or below those in the nearshore surficial sediments (Table 7). The Owen Sound WPCP sludge data generally fall at the low end of the concentrations of metals reported for other Ontario primary treatment plants (CAWPRC, 1987).

#### Solvent Extractables

Solvent extractables (oil and grease) were found in all samples, and concentrations tended to be higher at stations closer to shore. However, with the exception of the Owen Sound WPCP sewage sludge, concentrations in sediments were low (69 to 498 mg/kg) and well below the MOE dredge disposal guideline (Table 8).

#### Trace Organics

No PCNs were found in sediment or WPCP sludge samples (Table 8 and Appendix Tables B-1 and B-2) at a MDL of 20 µg/kg (Halowax 1099 standard). PCBs, OCs, CBs and PAHs were also absent from all samples. MDLs for these compounds are 20 µg/kg, 1 to 5 µg/kg, 1 to 2 µg/kg and 10 to 70 µg/kg, respectively.

### 6.0 CONCLUSIONS AND RECOMMENDATIONS

#### Polychlorinated Naphthalenes

Of the four point-source discharges sampled on October 18, PCNs were only found in the Goodyear V-Belt Plant final effluent (immediately after granular activated carbon treatment), at a level of 13 ng Halowax 1099/l. This suggests that the GAC treatment was not completely effective in removing PCNs.

No other Halowax formulations were detected in the Goodyear discharge. Although flow of this discharge was not continuous during the survey, if one uses the annual average daily flow of  $800 \times 10^3 \text{ m}^3/\text{d}$ , the above concentration of total PCNs would result in a daily loading of about 10 g/d that would not be detected with the routine 1 litre samples and MDL of 20 ng/l.



This, combined with the observed oily film in the discharge on the day following sampling, suggests that not all PCN sources have been eliminated. Weekly monitoring of the final discharge by MOE has found total PCN concentrations between 20 and 50 ng/l, and these detections are probably related to the sewer system purging itself of low-level residual contamination over time (W. Page, MOE, Owen Sound, pers. comm., 1991). It is recommended that, should there be a need to determine PCN loadings during this process, then periodic large volume sampling is advisable.

No PCNs were detected in any of the 1 litre (MDL = 20 ng/l) or 18 litre (MDL = 10 ng/l) water samples collected along the eastern shore of Owen Sound Harbour near the Goodyear plant. Consequently, there was no detectable impact of the Goodyear effluent on water quality during the survey (October 16-19). However, it should be noted that effluent discharge from the plant was on a batch (intermittent) basis at the time.

No PCNs were detected in surficial sediments (MDL = 20 µg/kg) collected upstream or downstream of the Goodyear facility, or in sewage sludge from the Owen Sound WPCP, which receives some cooling water from Goodyear. Given that earlier effluent samples from Goodyear contained much higher total PCN concentrations than that found during the survey, this indicates that the impact on nearby sediments was minimal.

PCNs were also not detected in sport fish from Owen Sound (D. Spry, MOE, internal memo, 1990). However, low concentrations of PCNs (18 to 42 ng/g, just slightly above the MDL) were detected in young-of-the-year forage fish collected at the 32nd St. E. storm sewer and at two locations NE of the Goodyear discharge in October, 1990 (K. Suns, MOE, pers. comm., 1990). Therefore, it is recommended that the caged mussels exposed during the study be analyzed to assist in further defining the impact of the Goodyear discharge on local biota.

#### Other Organochlorine Contaminants

Although PCBs, organochlorine pesticides and chlorinated benzenes were also analyzed for in the large volume point source and Owen Sound Harbour water samples, only low concentrations ( $\leq 2$  ng/l) of alpha- and gamma-BHC were found.



Concentrations of gamma-BHC (lindane) were below the objective for the protection of aquatic life. These two BHC isomers are relatively ubiquitous in the Great Lakes, and are even present in distilled water. Their presence therefore does not appear to imply a local source.

No PCBs, OCs or CBs were detected in any of the Owen Sound Harbour surficial sediment samples or in Owen Sound WPCP sewage sludge.

### **Polycyclic Aromatic Hydrocarbons**

Low concentrations (2-12 ng/l) of phenanthrene, fluoranthene, pyrene and benzo(a)anthracene were found in most of the large volume water samples from Owen Sound Harbour. The detection of higher concentrations of fluoranthene and pyrene in water near the Goodyear discharge, and the presence of the first three compounds in the Goodyear effluent and in the nearby 32nd St. E. storm sewer discharge suggests that these are the probable sources of the PAHs. However, the 10-fold higher MDLs for PAHs in the Kenny Drain and Owen Sound WPCP samples may have precluded the detection of PAHs in these discharges. The absence of guidelines for PAHs prevents interpretation of the significance of the Owen Sound Harbour water concentrations to local aquatic life. *However, it is recommended that tissues of the filter-feeding mussels exposed to these waters during the survey be analyzed to determine whether or not the PAHs are biologically available and constitute a problem.*

PAHs do not appear to be accumulating in the nearby sediments, since none were detected in any of the samples collected.

### **Nutrients and Trace Metals**

Concentrations of nutrients and trace metals in surficial sediments were quite low. Under the current MOE dredging guidelines, these sediments would be considered to be safe for open water disposal. Furthermore, the concentrations of trace metals are in the range considered as "background" for Great Lakes sediments. Nevertheless, phosphorus and nitrogen levels at more than 50% of the 14 stations sampled, as well as copper and nickel at some stations upstream of the Goodyear discharge, were slightly above the recently-proposed (draft) "lowest effect level" guidelines for the protection of the majority of sediment-dwelling organisms.



In laboratory tests, sediments from selected stations were not toxic to Hexagenia or Chironomus, and in fact supported good growth. There was, however, lethality to fathead minnow juveniles, which is thought to be due to ammonia released from the sediments (D. Spry, MOE, internal memo, 1990).

Although concentrations of many of the metals tended to be higher at stations closer to shore, Goodyear was not implicated as a source.

#### Other Parameters

Except for PAHs and solvent extractables, a spatial pattern in the distribution of trace organics was not evident in water or sediment samples, since, apart from BHCs in water, no other compounds were present at quantifiable levels.

On the other hand, elevated conductivity, suspended solids, calcium, chloride and dissolved organic carbon levels were found in nearshore waters after heavy rainfall events. This is indicative of the impact of sources south-west (upstream) of Goodyear on the nearshore aquatic environment. In particular, the Kenny Drain resulted in a significant nearshore turbidity plume that extended at least as far north as Squaw Point during the survey. *It is recommended that the impact of this periodic input of fine particulate matter on the nearshore aquatic environment and biota be investigated, and that measures to reduce the loading of particulates be initiated.*





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## APPENDICES

A - STATION LOCATIONS, SAMPLE DATES AND ANALYSIS

B & C - FIELD AND LABORATORY QUALITY ASSURANCE DATA





## **APPENDICES**

**A - STATION LOCATIONS, SAMPLE NUMBERS AND RAINFALL**

**B & C - FIELD AND LABORATORY QUALITY ASSURANCE DATA**





| Station | Sample | Rainfall | Location        | Remarks         |
|---------|--------|----------|-----------------|-----------------|
| 1       | 1      | 10       | 10 10 10 10     | 10 10 10 10     |
| 2       | 2      | 20       | 20 20 20 20     | 20 20 20 20     |
| 3       | 3      | 30       | 30 30 30 30     | 30 30 30 30     |
| 4       | 4      | 40       | 40 40 40 40     | 40 40 40 40     |
| 5       | 5      | 50       | 50 50 50 50     | 50 50 50 50     |
| 6       | 6      | 60       | 60 60 60 60     | 60 60 60 60     |
| 7       | 7      | 70       | 70 70 70 70     | 70 70 70 70     |
| 8       | 8      | 80       | 80 80 80 80     | 80 80 80 80     |
| 9       | 9      | 90       | 90 90 90 90     | 90 90 90 90     |
| 10      | 10     | 100      | 100 100 100 100 | 100 100 100 100 |
| 11      | 11     | 110      | 110 110 110 110 | 110 110 110 110 |
| 12      | 12     | 120      | 120 120 120 120 | 120 120 120 120 |
| 13      | 13     | 130      | 130 130 130 130 | 130 130 130 130 |
| 14      | 14     | 140      | 140 140 140 140 | 140 140 140 140 |
| 15      | 15     | 150      | 150 150 150 150 | 150 150 150 150 |
| 16      | 16     | 160      | 160 160 160 160 | 160 160 160 160 |
| 17      | 17     | 170      | 170 170 170 170 | 170 170 170 170 |
| 18      | 18     | 180      | 180 180 180 180 | 180 180 180 180 |
| 19      | 19     | 190      | 190 190 190 190 | 190 190 190 190 |
| 20      | 20     | 200      | 200 200 200 200 | 200 200 200 200 |
| 21      | 21     | 210      | 210 210 210 210 | 210 210 210 210 |
| 22      | 22     | 220      | 220 220 220 220 | 220 220 220 220 |
| 23      | 23     | 230      | 230 230 230 230 | 230 230 230 230 |
| 24      | 24     | 240      | 240 240 240 240 | 240 240 240 240 |
| 25      | 25     | 250      | 250 250 250 250 | 250 250 250 250 |
| 26      | 26     | 260      | 260 260 260 260 | 260 260 260 260 |
| 27      | 27     | 270      | 270 270 270 270 | 270 270 270 270 |
| 28      | 28     | 280      | 280 280 280 280 | 280 280 280 280 |
| 29      | 29     | 290      | 290 290 290 290 | 290 290 290 290 |
| 30      | 30     | 300      | 300 300 300 300 | 300 300 300 300 |

## APPENDIX A

### STATION LOCATIONS, SAMPLE NUMBERS AND RAINFALL

1. Station locations are given in Appendix A-1. The sample numbers are given in Appendix A-2. The rainfall data are given in Appendix A-3.





Appendix Table A-1. Owen Sound Harbour sampling station locations.

| Station |      | Distance in metres from: |           | Latitude     |              | Longitude |  | Remarks                                                     |
|---------|------|--------------------------|-----------|--------------|--------------|-----------|--|-------------------------------------------------------------|
| Number  | Type | East shore               | Goodyear  |              |              |           |  |                                                             |
| 1       | 9    | -60                      | 0         | 44 36' 14.0" | 80 55' 03.0" |           |  | Goodyear V-Belt Plant final effluent (after GAC treatment). |
| 1       | 5    | 0                        | 120; SW   | 44 36' 05.0" | 80 55' 06.0" |           |  | 32nd Street East storm sewer discharge.                     |
| 2       | 5    | -50                      | 690; SW   | 44 35' 54.0" | 80 55' 16.0" |           |  | Kenny Drain discharge.                                      |
| 2       | 3    | -50                      | 2270; SW  | 44 35' 09.0" | 80 55' 53.0" |           |  | Owen Sound Water Pollution Control Plant final effluent.    |
| 36      | 17   | 320                      | 320; NNW* | 44 36' 22.5" | 80 55' 10.5" |           |  |                                                             |
| 37      | 17   | 195                      | 190; NNW  | 44 36' 19.5" | 80 55' 08.0" |           |  |                                                             |
| 38      | 17   | 100                      | 100; NNW  | 44 36' 16.5" | 80 55' 05.5" |           |  |                                                             |
| 39      | 17   | 40                       | 0         | 44 36' 15.0" | 80 55' 03.5" |           |  |                                                             |
| 40      | 17   | 60                       | 120; NNE  | 44 36' 18.2" | 80 55' 01.8" |           |  |                                                             |
| 41      | 17   | 175                      | 190; N    | 44 36' 21.0" | 80 55' 03.9" |           |  |                                                             |
| 42      | 17   | 300                      | 340; NNW  | 44 36' 25.5" | 80 55' 07.9" |           |  |                                                             |
| 43      | 17   | 100                      | 320; NE   | 44 36' 24.5" | 80 54' 57.2" |           |  |                                                             |
| 44      | 17   | 300                      | 480; NNE  | 44 36' 30.0" | 80 55' 01.8" |           |  |                                                             |
| 45      | 17   | 400                      | 1075; NNE | 44 36' 49.5" | 80 54' 49.5" |           |  | near Squaw Point Shoal.                                     |
| 46      | 17   | 50                       | 120; WSW  | 44 36' 12.8" | 80 55' 06.5" |           |  | near 32nd Street East storm sewer.                          |
| 47      | 17   | 150                      | 150; WNW  | 44 36' 15.4" | 80 55' 09.0" |           |  |                                                             |
| 48      | 17   | 50                       | 360; SW   | 44 36' 05.0" | 80 55' 12.3" |           |  | near storm sewer; opposite industrial mall.                 |
| 49      | 17   | 50                       | 690; SSW  | 44 35' 55.5" | 80 55' 18.1" |           |  | near Kenny Drain; north of Hobart Mfg.                      |
| 50      | 17   | 880                      | 1300; WSW | 44 35' 57.5" | 80 55' 54.0" |           |  | near Owen Sound WTP intake.                                 |
| 51      | 17   | 10                       | 1100; NE  | 44 36' 42.0" | 80 54' 38.0" |           |  | in bay south of Squaw Point.                                |

- NOTES: 1) Distances are from Goodyear discharge, at point of entry to Owen Sound Harbour.  
2) Negative distances indicate that sampling point was on shore.  
3) \* = compass bearing, north-north west.

Appendix Table A-2. Owen Sound Harbour sample numbers.

| Station |      | Point Source   |       | Water               |                     | Water          | Sediment            | Sludge |
|---------|------|----------------|-------|---------------------|---------------------|----------------|---------------------|--------|
| Number  | Type | (large volume) |       | surface             | bottom              | (large volume) |                     |        |
| 1       | - 9  | Goodyear       | 56600 |                     |                     |                |                     |        |
| 2       | - 5  | 32nd St.E.SS   | 56599 |                     |                     |                |                     |        |
| 1       | - 5  | Kenny Drain    | 56598 |                     |                     |                |                     |        |
| 2       | - 3  | WPCP           | 56597 |                     |                     |                |                     | 46475  |
| 36      | 17   |                |       | 46073               | 46074               |                | 46461               |        |
| 37      | 17   |                |       | 46075               | 46076               |                | 46462               |        |
| 38      | 17   |                |       | 46077, 46078, 46079 | 46080, 46081        | 56590          | 46463, 46464, 46465 |        |
| 39      | 17   |                |       | 46089               | 46090               | 56589          | 46469               |        |
| 40      | 17   |                |       | 46097               | 46098               | 56591          | 46477, 46478, 46479 |        |
| 41      | 17   |                |       | 46082, 46083        | 46084, 46085, 46086 |                | 46466, 46467        |        |
| 42      | 17   |                |       | 46103               | 46104               |                | 46480               |        |
| 43      | 17   |                |       | 46101               | 46102               | 56592          | 46805               |        |
| 44      | 17   |                |       | 46093               | 46094               |                | 46473, 46474        |        |
| 45      | 17   |                |       | 46099               | 46100               | 56594          | 46806               |        |
| 46      | 17   |                |       | 46091               | 46092               | 56593          | 46470, 46471, 46472 |        |
| 47      | 17   |                |       | 46105               | 46106               |                | 46481, 46482, 46483 |        |
| 48      | 17   |                |       |                     |                     |                | 46808               |        |
| 49      | 17   |                |       |                     |                     |                | 46807               |        |
| 50      | 17   |                |       |                     |                     |                | 46809               |        |



Appendix Table A-3. Rainfall at Owen Sound during survey.

| Date       | * Rainfall, mm |      |       |
|------------|----------------|------|-------|
|            | 8 AM           | 4 PM | Total |
| October 15 | 9.6            | 0.0  | 9.6   |
| October 16 | 0.0            | 0.0  | 0.0   |
| October 17 | 5.8            | 4.8  | 10.6  |
| October 18 | 3.2            | 4.6  | 7.8   |
| October 19 | 3.6            | 0.0  | 3.6   |

\* Data from Environment Canada, Atmospheric Environment Service, Toronto, Ont.

## APPENDIX B

### **FIELD AND LABORATORY QUALITY ASSURANCE DATA FOR WATER**

Field water sample quality assurance data (Appendix Table B-1) showed that the variability between blind duplicates was, with one exception, quite low (i.e., less than 10% of the mean) and very similar to laboratory variability for duplicate analyses. This suggests that most of the observed differences between pairs of samples is attributable to analytical variability. In the case of suspended solids, however, the much higher field variability (up to 21%) compared to laboratory variability (8.6%) suggests that there are inherent difficulties or inadequacies in obtaining a representative duplicate sample for this parameter.

Although no field (distilled water) blank samples were collected for conventional parameters, no PCNs were detected in field blanks (Appendix Table B-2). Travel blank data were similar to those for laboratory blanks. Generally, concentrations in travel blanks were less than 6% of the levels measured in actual samples (Table 4). In the case of dissolved organic carbon, however, the distilled water concentration was as high as 29% of the lowest measured field concentration. With few exceptions, PCBs, OCs and CBs were not detected in a large volume distilled water blank. Of those compounds found, dieldrin and 2,6,a-trichlorotoluene were present at or near their respective MDLs; hexachloroethane was below its MDL (trace); and levels of alpha- and gamma BHC were similar to those found in effluent and water samples (Appendix Table B-2).

Within-station heterogeneity, as measured by triplicate water samples taken in close succession to one another, was, in most cases very similar to laboratory variability for controls or standards, and did not exceed 15% (Appendix Table B-3). Field replicate variability for suspended solids, however, was far greater than analytical (up to 34.6% vs. 0.005%). This difference alludes to the difficulty of obtaining a representative duplicate sample (see above and Appendix Table B-1).



Appendix Table B-1. Owen Sound Harbour water blind duplicate (split) data.

| Parameter                        | Station 41 |       | Station 38 |       | Variability (CV), % |               |
|----------------------------------|------------|-------|------------|-------|---------------------|---------------|
|                                  | 46082      | 46083 | 46080      | 46081 | Field *             | Laboratory ** |
| Conductivity, us/cm @25C         | 193        | 192   | 230        | 223   | 0.4 to 2.2          | 0.9 to 1.9    |
| Calcium, mg/l                    | 26.28      | 26.65 | 32.33      | 30.37 | 1.0 to 4.4          | 2.0           |
| Chloride, mg/l                   | 5.00       | 4.90  | 8.00       | 7.30  | 1.4 to 6.5          | 2.3           |
| Dissolved Organic Carbon, mg/l   | 1.6        | 1.6   | 2.4        | 2.2   | 0.0 to 6.1          | 5.7 to 10.9   |
| Suspended Solids, mg/l           | 2.8        | 3.3   | 1.7<T      | 2.3<T | 11.6 to 21.2        | 8.6           |
| Total PCNs as Halowax 1099, ng/l | <20<W      | <20<W | <20<W      | <20<W | NA                  | 4.7           |

NOTES: CV = coefficient of variation, (Std.Dev./Mean) x 100.

\* calculated using  $CV = \left[ \sqrt{2} \frac{(\max. - \min.)}{(\max. + \min.)} \right] \times 100$ .

\*\* data from Sturgis (1987) and for PCNs, from MOE (1990b).

<T = a measurable trace amount; interpret with caution.

<W = no measurable response (zero); less than reported value.

NA = not available or could not be calculated.

Appendix Table B-2. Owen Sound Harbour water blank data.

| Parameter                             | MDL | Field Blanks |         |          | Travel Blank | Laboratory |
|---------------------------------------|-----|--------------|---------|----------|--------------|------------|
|                                       |     | 46107 *      | 46108 * | 67230 ** | 35369 *      | Blanks *** |
| Conductivity, us/cm @25 C             | 0.2 | NA           | NA      |          | 3            | NA         |
| Calcium, mg/l                         | 0.1 | NA           | NA      |          | <0.10<W      | 0.01       |
| Chloride, mg/l                        | 0.2 | NA           | NA      |          | <0.20<T      | 0.10       |
| Dissolved Organic Carbon, mg/l        | 1   | NA           | NA      |          | 0.4<T        | 0.0        |
| Suspended Solids, mg/l                | 0.5 | NA           | NA      |          | <0.5<W       | 0.31       |
| Total PCNs as Halowax 1099, ng/l      | 20  | <20<W        | <20<W   | NA       | <20<W        | <20<W      |
| PCBs/Organochlorine Pesticides, ng/l: |     |              |         |          |              |            |
| Total PCBs                            | 10  |              |         | nd       |              |            |
| Aldrin                                | 0.1 |              |         | nd       |              |            |
| Dieldrin                              | 0.2 |              |         | 0.2      |              |            |
| alpha-BHC                             | 0.1 |              |         | 0.8      |              |            |
| beta-BHC                              | 0.1 |              |         | nd       |              |            |
| gamma-BHC (Lindane)                   | 0.1 |              |         | 0.3      |              |            |
| alpha-Chlordane                       | 0.2 |              |         | nd       |              |            |
| gamma-Chlordane                       | 0.2 |              |         | nd       |              |            |
| p,p-DDD                               | 0.5 |              |         | nd       |              |            |
| p,p'-DDE                              | 0.1 |              |         | nd       |              |            |
| o,p'-DDT                              | 0.5 |              |         | nd       |              |            |
| p,p'-DDT                              | 0.5 |              |         | nd       |              |            |
| Endrin                                | 0.4 |              |         | nd       |              |            |
| alpha-Endosulphan                     | 0.2 |              |         | nd       |              |            |
| beta-Endosulphan                      | 0.4 |              |         | nd       |              |            |
| Endosulphan Sulphate                  | 0.4 |              |         | nd       |              |            |
| Heptachlor                            | 0.1 |              |         | nd       |              |            |
| Heptachlor epoxide                    | 0.1 |              |         | nd       |              |            |
| Oxychlordane                          | 0.2 |              |         | nd       |              |            |
| Methoxychlor (DMDT)                   | 0.4 |              |         | nd       |              |            |
| Mirex                                 | 0.5 |              |         | nd       |              |            |
| Chlorobenzenes, ng/l:                 |     |              |         |          |              |            |
| Hexachlorobutadiene (HCBD)            | 0.1 |              |         | nd       |              |            |
| Hexachloroethane (HCE)                | 0.1 |              |         | TR(0.02) |              |            |
| Pentachlorobenzene (QCB)              | 0.1 |              |         | nd       |              |            |
| Hexachlorobenzene (HCB)               | 0.1 |              |         | nd       |              |            |
| 1,2,3,4-Tetrachlorobenzene (TeCB)     | 0.1 |              |         | nd       |              |            |
| 1,2,3,5-Tetrachlorobenzene            | 0.1 |              |         | nd       |              |            |
| 1,2,4,5-Tetrachlorobenzene            | 0.1 |              |         | nd       |              |            |
| 1,2,3-Trichlorobenzene (TCB)          | 0.1 |              |         | nd       |              |            |
| 1,2,4-Trichlorobenzene                | 0.2 |              |         | nd       |              |            |
| 1,3,5-Trichlorobenzene                | 0.2 |              |         | nd       |              |            |
| 2,3,6-Trichlorotoluene (TCT)          | 0.1 |              |         | nd       |              |            |
| 2,4,5-Trichlorotoluene                | 0.1 |              |         | nd       |              |            |
| 2,6,a-Trichlorotoluene                | 0.1 |              |         | 0.2      |              |            |
| Octachlorostyrene (OCS)               | 0.1 |              |         | nd       |              |            |

NOTES: MDL = method detection limit.

\* conventional samples.

\*\* large volume (18 l) sample from Don R. study.

\*\*\* data from Sturgis (1987) and for PCNs, from MOE (1990b).

&lt;T = a measurable trace amount; interpret with caution.

&lt;W = no measurable response (zero); less than reported value.

NA = not available.



Appendix Table B-3. Owen Sound Harbour water replicate data.

| Parameter                        | Station 41 |       |       | Station 38 |       |       | Variability (CV), % |              | Analytical *<br>Recovery, % |
|----------------------------------|------------|-------|-------|------------|-------|-------|---------------------|--------------|-----------------------------|
|                                  | 46084      | 46085 | 46086 | 46077      | 46078 | 46079 | Field               | Laboratory * |                             |
| Conductivity, us/cm @25C         | 192        | 192   | 191   | 238        | 238   | 240   | 0.3 to 0.4          | 5.2          | NA                          |
| Calcium, mg/l                    | 26.74      | 26.50 | 26.63 | 32.40      | 32.94 | 33.12 | 0.5 to 1.1          | 1.3          | NA                          |
| Chloride, mg/l                   | 4.90       | 4.90  | 4.90  | 8.00       | 8.50  | 8.20  | 0.0 to 3.1          | 2.9          | NA                          |
| Dissolved Organic Carbon, mg/l   | 1.5        | 1.8   | 1.7   | 3.1        | 3.2   | 2.4   | 9.2 to 15.0         | 2.6 to 8.0   | NA                          |
| Suspended Solids, mg/l           | 1.8<T      | 1.4   | 1.4<T | 2.0<T      | 2.0<T | 3.5   | 15.1 to 34.6        | 0.005        | 98.5                        |
| Total PCNs as Halowax 1099, ng/l | <20<W      | <20<W | <20<W | <20<W      | <20<W | <20<W | 0.0                 | NA           | 90.5                        |

NOTES: CV = coefficient of variation, (Std.Dev./Mean) x 100.

\* data from Sturgis (1987) and for PCNs, from MOE (1990b).

<T = a measurable trace amount; interpret with caution.

<W = no measurable response (zero); less than reported value.

NA = not available or could not be calculated.





## APPENDIX C

### **FIELD AND LABORATORY QUALITY ASSURANCE DATA FOR SEDIMENT**

The sediment quality assurance data showed that, for those parameters present at levels well above their respective detection limits, the maximum variability between field blind duplicates was usually less than 15% of the mean, and similar to laboratory variability for duplicate analyses (Appendix Table C-1). This suggests that for nitrogen, phosphorus, arsenic, chromium, copper, iron, nickel and possibly mercury as well, most of the observed differences between pairs of samples is due to analytical variability. On the other hand, for parameters present at low concentrations or percentages (2,000 to 1,000  $\mu\text{m}$ , <62  $\mu\text{m}$ , loss on ignition, total organic carbon, cadmium, lead and zinc), the upper coefficient of field variation ranged from 16.1% to 141%, suggesting that there are difficulties in obtaining representative duplicate samples for these parameters. Solvent extractables were an exception to the above trend: even though present at levels considerably above the MDL, variability between duplicates was up to 43.9%.

Unfortunately, no conclusions can presently be made regarding the possible reasons for the high variability of solvent extractables and of particle size data, since no comparable laboratory coefficient of variation data was available.

Long-term laboratory blank data for trace metals (Appendix Table C-1) in general indicates low analytical contributions to observed sediment concentrations (Table 7), ranging from 0% to 17% for arsenic, chromium, iron, mercury and nickel. For cadmium, copper, lead and zinc, this "background" may have contributed from 26% to 100% of the lowest observed concentrations, thereby making data for these parameters less reliable.

For some of the nutrient and the trace element parameters, laboratory variability for the repeated analysis of controls or standards was similar to laboratory variability for duplicate analyses (Appendix Table C-1), but less than that for field replicates (Appendix Table C-2). This suggests that for loss on ignition, total organic carbon, nitrogen, phosphorus, cadmium, lead and mercury and possibly solvent extractables as well, the higher field variability at some stations (ranging up to 173%) is related to within-station heterogeneity and therefore, real differences between samples. However, in view of the



substantial variability between field split samples for total organic carbon, lead, mercury and solvent extractables (Appendix Table C-1), this may, in fact be due to difficulties in obtaining a representative sample. Furthermore, for arsenic, chromium, copper, iron, nickel and zinc, the similar or somewhat higher laboratory "repeat" analysis variability suggests that a good deal of the observed variability within stations may be accounted for by laboratory variability (Appendix Table C-2).



Appendix Table C-1. Owen Sound Harbour sediment blind duplicate (split) data.

| Parameter                         | Station 44 |          | Station 41 |          | Variability (CV), % |               | Laboratory Blank ** |
|-----------------------------------|------------|----------|------------|----------|---------------------|---------------|---------------------|
|                                   | 46473      | 46474    | 46466      | 46467    | Field *             | Laboratory ** |                     |
| Particle Size:                    |            |          |            |          |                     |               |                     |
| 2000 to 1000 um, %                | 0.00       | 0.00     | 0.10       | 0.00     | 0.0 to 141          | NA            | NA                  |
| 999 to 62 um, %                   | 92.80      | 93.60    | 87.00      | 83.50    | 0.6 to 2.9          | NA            | NA                  |
| <62 um, %                         | 7.12       | 6.37     | 12.89      | 16.31    | 6.3 to 16.6         | NA            | NA                  |
| Loss on Ignition, g/kg            | 3.9        | 4.9      | 7.9        | 7.9      | 0.0 to 16.1         | 6.6           | NA                  |
| Total Organic Carbon, g/kg        | <0.20<W    | <0.20<W  | 1.90       | <0.20<W  | 0.0 to 141          | 3.2           | NA                  |
| Total Kjeldahl Nitrogen, g/kg     | 0.35       | 0.38     | 0.37       | 0.32     | 5.8 to 10.2         | 4.9           | NA                  |
| Total Phosphorus, g/kg            | 0.68       | 0.80     | 0.60       | 0.52     | 10.1 to 11.5        | 6.0           | NA                  |
| Arsenic, mg/kg                    | 1.30       | 1.20     | 1.50       | 1.50     | 0.0 to 5.7          | 12.1          | 0.00                |
| Cadmium, mg/kg                    | 0.42       | 0.37     | 0.16<T     | 0.12<T   | 9.0 to 20.2         | 12.8          | 0.04                |
| Chromium, mg/kg                   | 18.00      | 16.00    | 11.00      | 11.00    | 0.0 to 8.3          | 10.7          | 1.60                |
| Copper, mg/kg                     | 6.10       | 6.50     | 8.90       | 9.40     | 3.9 to 4.5          | 9.4           | 1.26                |
| Iron, mg/kg                       | 22000.00   | 20000.00 | 11000.00   | 12000.00 | 6.1 to 6.7          | 3.2           | 1.80                |
| Lead, mg/kg                       | 2.30<T     | <1.00<W  | 2.30<T     | <1.00<W  | 0.0 to 141          | 7.8           | 1.33                |
| Mercury, mg/kg                    | <0.01<W    | <0.01<W  | <0.01<W    | <0.01<W  | 0.0                 | 10.6          | NA                  |
| Nickel, mg/kg                     | 8.90       | 8.70     | 9.50       | 9.70     | 1.5 to 1.6          | 5.1           | 0.98                |
| Zinc, mg/kg                       | 25.00      | 19.00    | 18.00      | 18.00    | 0.0 to 19.3         | 9.5           | 7.32                |
| Solvent Extractables, mg/kg       | 87         | 165      | 270        | 227      | 12.2 to 43.8        | NA            | NA                  |
| Total PCNs as Halowax 1099, ug/kg | <20<W      | <20<W    | NA         | NA       | 0.0                 | NA            | NA                  |

NOTES: CV = coefficient of variation, (Std.Dev./Mean) x 100.

\* calculated using  $CV = [\sqrt{2} (\max. - \min.) / (\max. + \min.)] \times 100$ .

\*\* data from Sturgis (1987) and for PCNs, from MOE (1990b).

&lt;T = a measurable trace amount; interpret with caution.

&lt;W = no measurable response (zero); less than reported value.

NA = not available or could not be calculated.

Appendix Table C-2. Owen Sound Harbour sediment replicates data.

| Parameter                          | Station 40 |          |          |          | Station 38 |          |          |          | Station 46 |         |         |         | Station 47    |              |      |  | Variability (CV), % |  | Analytical *<br>Recovery, % |
|------------------------------------|------------|----------|----------|----------|------------|----------|----------|----------|------------|---------|---------|---------|---------------|--------------|------|--|---------------------|--|-----------------------------|
|                                    | 46477      | 46478    | 46479    | 46483    | 46464      | 46465    | 46470    | 46471    | 46472      | 46481   | 46482   | 46483   | Field         | Laboratory * |      |  |                     |  |                             |
| Particle Size:                     |            |          |          |          |            |          |          |          |            |         |         |         |               |              |      |  |                     |  |                             |
| 2000 to 1000 um, %                 | 0.10       | 0.10     | 0.00     | 0.10     | 0.10       | 0.10     | 0.30     | 0.10     | 0.30       | 0.00    | 0.00    | 0.10    | 0.0 to 173.2  | NA           | NA   |  |                     |  |                             |
| 999 to 62 um, %                    | 81.60      | 82.00    | 68.90    | 82.70    | 87.50      | 87.80    | 39.20    | 55.50    | 48.40      | 84.00   | 84.40   | 87.10   | 2.0 to 17.1   | NA           | NA   |  |                     |  |                             |
| <62 um, %                          | 18.15      | 17.81    | 30.86    | 17.14    | 12.28      | 12.06    | 56.64    | 44.12    | 51.08      | 15.79   | 15.53   | 12.65   | 11.9 to 33.4  | NA           | NA   |  |                     |  |                             |
| Loss on Ignition, g/kg             |            |          |          |          |            |          |          |          |            |         |         |         |               |              |      |  |                     |  |                             |
| Total Organic Carbon, g/kg         | 5.30       | 5.00     | 3.6      | 3.70     | 5.70       | 1.10     | 14.00    | 11.00    | 18.00      | 4.60    | 5.40    | 4.20    | 12.9 to 65.9  | 2.7          | NA   |  |                     |  |                             |
| Total Kjeldahl Nitrogen, g/kg      | 0.69       | 0.75     | 0.75     | 0.62     | 0.46       | 0.50     | 1.10     | 0.91     | 1.10       | 0.63    | 0.62    | 0.55    | 4.7 to 15.8   | 4.9          | NA   |  |                     |  |                             |
| Total Phosphorus, g/kg             | 0.64       | 0.76     | 0.73     | 0.68     | 0.58       | 0.69     | 0.60     | 0.66     | 0.66       | 0.51    | 0.48    | 0.57    | 5.4 to 9.4    | 3.5          | NA   |  |                     |  |                             |
| Arsenic, mg/kg                     |            |          |          |          |            |          |          |          |            |         |         |         |               |              |      |  |                     |  |                             |
| Cadmium, mg/kg                     | 1.70       | 1.90     | 1.70     | 2.10     | 2.10       | 2.00     | 2.60     | 2.40     | 2.60       | 2.10    | 1.90    | 2.00    | 2.8 to 6.5    | 14.3         | NA   |  |                     |  |                             |
| Chromium, mg/kg                    | 0.36       | 0.49     | 0.40     | 0.23<T   | 0.26       | 0.46     | 0.52     | 0.53     | 0.34       | 0.32    | 0.33    | 0.10<T  | 16.0 to 52.0  | 6.5          | NA   |  |                     |  |                             |
| Copper, mg/kg                      | 15.00      | 13.00    | 12.00    | 12.00    | 12.00      | 13.00    | 15.00    | 15.00    | 15.00      | 9.30    | 9.70    | 9.40    | 0.0 to 11.5   | 11.6         | NA   |  |                     |  |                             |
| Iron, mg/kg                        | 12.00      | 11.00    | 11.00    | 10.00    | 8.20       | 8.90     | 16.00    | 16.00    | 18.00      | 11.00   | 12.00   | 10.00   | 6.9 to 10.0   | 9.7          | NA   |  |                     |  |                             |
| Lead, mg/kg                        | 13000.00   | 13000.00 | 12000.00 | 14000.00 | 13000.00   | 14000.00 | 13000.00 | 14000.00 | 14000.00   | 7800.00 | 8200.00 | 8200.00 | 2.9 to 4.6    | 4.7          | NA   |  |                     |  |                             |
| Mercury, mg/kg                     | 7.20       | 1.30<T   | 2.60<T   | 1.90<T   | <1.00<W    | <1.00<W  | 6.10     | 3.30<T   | <1.00<W    | 4.20<T  | 3.00<T  | 1.00<W  | 83.8 to 173.2 | 10.1         | NA   |  |                     |  |                             |
| Nickel, mg/kg                      | <0.01<W    | <0.01<W  | <0.01<W  | <0.01<W  | <0.01<W    | <0.01<W  | 0.02<T   | <0.01<W  | <0.01<W    | <0.01<W | 0.02<T  | <0.01<W | 0.0 to 173.2  | 7.6          | NA   |  |                     |  |                             |
| Zinc, mg/kg                        | 11.00      | 11.00    | 11.00    | 11.00    | 9.60       | 10.00    | 15.00    | 15.00    | 15.00      | 10.00   | 11.00   | 9.50    | 0.0 to 7.5    | 10.0         | NA   |  |                     |  |                             |
| Solvent Extractables, mg/kg        | 25.00      | 26.00    | 25.00    | 21.00    | 19.00      | 20.00    | 34.00    | 30.00    | 30.00      | 22.00   | 20.00   | 19.00   | 2.3 to 7.5    | 9.7          | NA   |  |                     |  |                             |
| Total PCNs as Halowax 1099, ug/kg; | 270        | 380      | 199      | 208      | 239        | 262      | 587      | 445      | 473        | 149     | 322     | 177     | 11.5 to 43.0  | NA           | NA   |  |                     |  |                             |
|                                    | <20<W      | <20<W    | <20<W    | -        | -          | -        | <20<W    | <20<W    | <20<W      | <20<W   | <20<W   | <20<W   | 0.0           | NA           | 94.0 |  |                     |  |                             |

NOTES: CV = coefficient of variation, (Std.Dev./Mean) x 100.

\* data from Sturgis (1987) and for PCNs, from MOE (1990b).

<T = a measurable trace amount.

<W = no measurable response (zero); less than reported value.

NA = not available or could not be calculated.



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